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Assessment of Waste Management of Volatile Radionuclides

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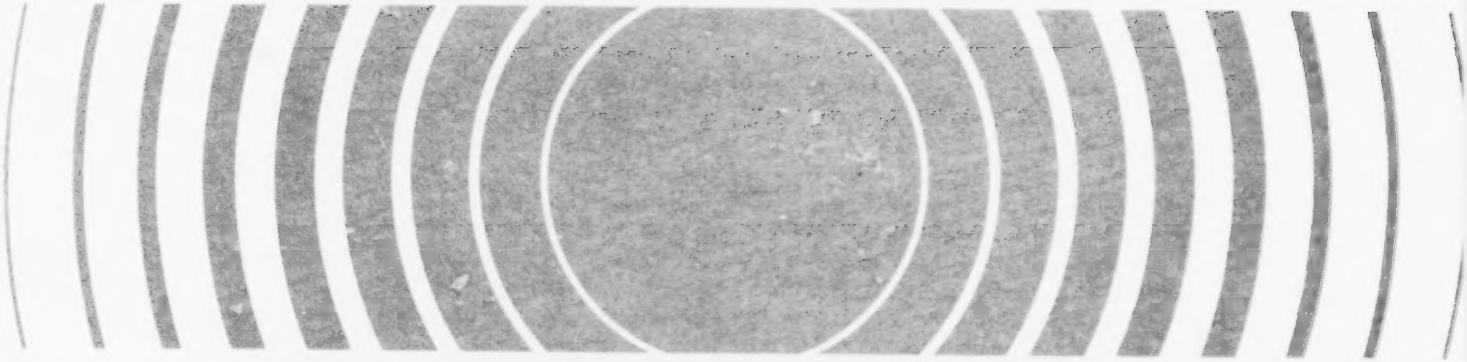

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FOREWORD

The Office of Radiation Programs carries out a national program designed to evaluate the exposure of man to ionizing and nonionizing radiation, and to promote the development of controls necessary to protect the public health and safety, and to assure environmental quality.

Regulations which will become effective in 1983 limit the release of the volatile radionuclides krypton-85 and iodine-129 into the general environment from uranium fuel cycle (UFC) operations. This contract report considers the problems of, and technologies for, the disposal of krypton-85 and iodine-129 collected in accordance with the UFC regulations. It also considers the disposal of two other volatile radionuclides, hydrogen-3 (tritium) and carbon-14. The information in this report will be used by the Agency in its development of standards for the management and disposal of high-level radioactive wastes.

Comments on this report are welcome; they may be sent to the Director, Criteria and Standards Division (ANR-460), Office of Radiation Programs, U.S. Environmental Protection Agency, Washington D.C., 20460

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ABSTRACT

This document presents a review of the Technologies for Waste Management of the Volatile Radionuclides of Iodine-129, Krypton-85, Tritum, and Carbon-14. The report presents an estimate of the quantities of these volatile radionuclides as are produced in the nuclear power industry. The various technologies as may be used, or which are under investigation, to immobilize these nuclides and to contain them during storage, and in disposal are discussed. Also, the alternative disposal options as may be applied to isolate these radioactive waste from the human environment are presented.

The report contains information which was available through approximately January of 1978.

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1.0 INTRODUCTION

This study, sponsored by the Environmental Protection Agency (EPA), Office of Radiation Protection (ORP) investigates control technologies and waste management for the radionuclides I-129, Kr-85, C-14, and H-3, as well as other volatile radionuclides which are released as gases or in volatile forms from nuclear facilities. This report is a survey of existing literature and provides background information to assist EPA in the preparation of standards for radioactive waste disposal of these volatile radionuclides.

In present U.S. defense related programs and proposed commercial nuclear programs, spent fuel from nuclear power reactors may be reprocessed to recover usable uranium and plutonium. During these chemical processing operations, radioactive gases, particulates, and volatile compounds are released to the off-gas effluent streams. Control approaches consisting of treatment of the off-gas streams to remove particulates and effluent gases, and atmospheric dispersion have been used in the nuclear industry to maintain radiation levels below applicable standards. Although the present control technology is capable of meeting or exceeding the requirements of maximum allowable radionuclide concentration standards, concern remains as to the release of the long half-life radionuclides. The long half-life volatile radionuclides, specifically iodine-129 (1.7×10^7 yr), krypton-85 (10.44 yr), carbon-14 (5,570 yr), and tritium (12.26 yr), have the potential to accumulate in the environment, presenting a long-term radiological hazard.

EPA recently promulgated standards, Title 40 Part 190, Code of Federal Regulations, limiting the allowable release of I-129, Kr-85, and the transuranium elements from the uranium fuel cycle. These uranium fuel cycle standards include limits of releases from milling operations through fuel element reprocessing operations.* Standards for limits on the allowable releases of carbon-14 and tritium are also under consideration. EPA is in the process of developing environmental standards for the "back end" of the fuel cycle, namely, the disposal of radioactive waste. Standards for radioactive waste disposal would include the portions of the nuclear fuel cycle following reprocessing through ultimate disposal--immobilization or solidification, packaging or containment, interim storage, and final disposal.

The primary emphasis of the present study is to describe current technologies for immobilization and containment of the collected volatile radionuclides. To provide a perspective of overall waste management, consideration is given to the quantities of waste that may be produced, physical and chemical form of the collected waste, immobilization and containment technologies, alternative disposal options, and environmental transport at each waste management stage. Although this report addresses each of these areas, the discussion

*Reprocessing operations may be interpreted to include additional waste treatment when performed onsite, e.g., immobilization or solidification of waste and packaging.

of waste management practices or alternatives remains incomplete and uncertain in some areas since relevant technologies for waste management of the volatile radionuclides are still being developed.

The primary source of volatile radionuclide release in the nuclear fuel cycle is from the spent fuel reprocessing operations. The exception to this would be in the case of a U.S. policy decision not to perform reprocessing and to directly dispose of spent fuel elements without recovery of uranium or plutonium. In this event, the primary release of the volatile radionuclides would occur sometime after disposal, if the integrity of the fuel elements and other engineered containment barriers were to fail.

At present there are no operating commercial spent fuel reprocessing plants in the U.S., although three reprocessing plants have been constructed. A reprocessing plant was operated by Nuclear Fuel Services at West Valley, New York. This plant was closed when it was determined that modifications would be required which were uneconomical for continued operation. The Midwest Fuel Recovery Plant was constructed at Morris, Illinois. Operational problems were encountered at this facility, requiring major plant modifications. No decision has been made to perform these modifications and the plant is presently being used for storage of spent fuel elements. A reprocessing plant was constructed by Allied-General Nuclear Services at Barnwell, South Carolina and licensing processes were initiated for this plant.

A U.S. Administration policy decision has been made not to proceed with commercial fuel reprocessing until issues of proliferation of nuclear materials are resolved.[1] In view of this decision, the future of the nuclear fuel reprocessing industry is not clear. In the interim, the U.S. Government is developing a program for the acceptance and caretaker responsibilities for spent fuel from privately owned nuclear reactors. No decision has been made as to whether such commercial fuel reprocessing will be performed at some future date or whether spent fuel elements will be disposed of as nuclear waste products.

Although reprocessing of commercial spent fuel will not occur unless a U.S. policy change is made, reprocessing is continuing for defense-related programs. Accordingly, the assessment of the waste management technology for volatile radionuclides remains of concern to assure protection of the environment and public welfare.

2.0 SUMMARY

The present study is a survey of the existing literature and provides background information for the preparation of standards for radioactive waste disposal. The present technologies for immobilization and containment of the long-lived volatile radionuclides (iodine-129, tritium, krypton-85, and carbon-14) are described, and the quantities produced, physical and chemical forms of the collected waste, alternative disposal options, and environmental transport are reviewed. Actual experience with control technologies is scarce because there are no operating commercial spent fuel reprocessing plants in the U.S.; the present national policy is to postpone commercial fuel reprocessing until issues of proliferation of nuclear materials are resolved. Concerning the assessment of waste management technology remains of concern to assure protection of the environment and the public welfare.

2.1 Quantities of Waste Produced

The quantities of radionuclides produced depend on the installed nuclear electric power generation capacity. The estimated gross nuclear power capacity in the year 2010 varies from 400 to 1000 GWe. The high-level radioactive waste from fuel reprocessing amounts to 3.3 percent of the heavy metal weight. Roughly 3.3 percent of the spent fuel will have to be disposed of after 10 years' aging. In this report, a model fuel reprocessing plant is assumed to be capable of handling 5MT of spent fuel per day. From 5 to 14 such plants may be required by the early part of the next century.

Iodine-129 is produced primarily as a fission product and through the decay of other fission products. A model reprocessing plant of the type referred to would release 380kg (or 66 Ci) of I-129 per year, mixed with about 250kg of stable I-127. Most of the iodine is released in elemental form, with 1 to 5 percent in organic form. The mercury, iodox, and chemisorption processes can be used for the collection of iodine.

Tritium (H-3) is produced primarily by ternary fission. Small amounts of H-3 can be produced by (n,n) reaction on Li-7 arising from the (n,α) reaction on B-10 used as a neutron adsorber in light water reactors (LWRs). The model reprocessing plant releases 1.25 x 10^6 Ci of H-3 per year. The chemical state in which tritium is released is not well established but it is known that tritium can occur in elemental form as tritiated water and also in combination with organic materials. The collection of tritium is accomplished through three processes:

(a) head end process, including voloxidation and pyrochemical techniques;

(b) process-stream, controls followed by isotopic separation;

(c) retention of entire water effluents, including wastes removed from gas stream.

Krypton-85 is the only noble gas radionuclide which is sufficiently long-lived to be important from a fuel processing standpoint. The annual production of krypton from the reference model reprocessing plant is about 143 m^3, of which approximately six percent will

be Kr-85 with an activity of 12.7 x 10^6 curies. Krypton is separated from other gaseous effluents by cryogenic distillation. Adsorbtion in fluorocarbons, liquid carbon dioxide, and on charcoal are also being investigated.

Carbon-14 is produced mainly by (n,p) reaction with N-14 (present in fuel as an impurity) and (n,α) reaction with O-17, and to a small extent by neutron capture in C-13. The amount of activity released from the model (5MT/day) processing plant is comparatively small, about 850 Ci/year. Most of the carbon released from the plant is in the form of CO_2. The best known method for the immobilization of carbon dioxide is caustic scrubbing with $Ca(OH)_2$ to form calcium carbonate. Adsorption on molecular sieves and in fluorocarbons has also been demonstrated on an experimental basis.

2.2 Available Immobilization Technology

To isolate the volatile radionuclides from the bio-sphere, four types of barriers are possible:

- the chemical form of the waste;
- immobilization in a solid matrix;
- outer containment;
- structural or natural barriers at storage or disposal sites.

In cases where there is a choice of various chemical compounds it would be prudent to choose the form which has the lowest solubility and leachability. Iodine-129 poses a special problem because of

its extremely long half-life. Incorporation of barium iodate in concrete has been particularly favored as an immobilization technique. Various experiments have been conducted to develop a model of the leaching of barium iodate from concrete, however, a universally applicable model is not yet available. Iodine can also be immobilized in zeolites, of which silver-exchanged zeolites have been found to have a high chemisorption capacity for elemental iodine. However, because of the high cost of silver chemisorption, lead exchanged zeolites are being investigated. No leaching tests are available on either type of iodine loaded zeolite.

For the containment of tritium, there is a choice between chemical storage and containment. Chemical storage technologies include the use of polymer-impregnated hydrates, organic compounds, and hydrides. Polymer-impregnated tritiated concrete has been the subject of several leaching studies and cost analyses. A method for the containment of tritiated water mixed with plaster and cement in a polyethylene drum resulted in very low leach rates. Organic compounds used for fixing tritium include bakelite, poly-acrylonitrile, and polystyrene. Also zirconium hydride has been found to be an adequate storage mechanism with a low leak rate.

Krypton, being a noble gas, is released in elemental form. Pressure vessel containment is the easiest method of storing krypton. Five hundred years has been suggested as a minimum for the useful life of each cylinder which can store krypton at a pressure of 120

atmospheres. The main reasons for possible failure of the vessel are heat released during radioactive decay and corrosion caused by the decay product rubidium. Krypton can also be stored by adsorption in zeolites and this method of containment has reached an advanced stage of development with a possible saturation sorbency of 45 litres per kilogram. Another method for immobilization of krypton is through ion implantation or sputtering on solids such as aluminum, but the amounts of metal required are too high to be practical. Much higher loadings have been achieved by electro-static acceleration of krypton ions. Methods for using metal matrices to hold granules of calcines containing krypton are also being studied. The only technique being studied for the immobilization of C-14 is the incorporation of $CaCO_3$ into concrete, asphalt, or polymers.

Table I is a summary for the waste radionuclides of the following:

- quantities produced (for model plant)
- available collection technology
- available immobilization technology
- containment packaging

2.3 Disposal Options

The following alternatives are considered for the disposal of volatile radionuclides:

- Geological repositories in salt beds, salt domes, and crystalline rock forms such as granite, basalt, shales, limestones, and clay beds. Of these, salt deposits have received the most attention because of their plastic flow properties. The greatest concern is groundwater movement.

TABLE I

PREPARATION OF VOLATILE RADIONUCLIDES FOR STORAGE/DISPOSAL

	NUCLIDES	IODINE-129	TRITIUM	KRYPTON-85	CARBON-14
	QUANTITIES PRODUCED (1)	66 Ci 380 kg .08 m^3 (2)	1.25 x 10^6 Ci 0.126 kg 1.2 litres (3)	12.7 x 10^6 Ci 530 kg 143 m^3 with 6% Kr-85	850 Ci 0.192 kg 300 litres (4)
COLLECTION TECHNOLOGY	COLLECTION METHOD(S)	Mercurex Iodox Chemisorption	Voloxidation Pyrochemical processes Process-Steam treatment	Cryogenic Distillation	Caustic scrubbing.
	COLLECTED FORM	Iodate of Hg, Ba	Tritiated water	Elemental	$CaCO_3$
	STATE OF DEVELOPMENT	Experimental	Early stages	Pilot plant	Well established for stable carbon.
	COST	Not known			\$0.15 per kg of CO_2 fixed.
IMMOBILIZATION TECHNOLOGY	IMMOBILIZED FORM	Iodate in concrete Zeolite	Chemical storage in polymer impregnated concrete, polyethylene Organic compounds Hydrides	Zeolite adsorption Ion implantation (sputtering)	$CaCO_3$ in concrete.
	LEACH RATE	Concrete leaching A cube 6000 kg leached in 17,000 years.	Around 0.0001% per year Zirconium hydride leaching .89 to 1.7 x 10^{-6} cm/day	0.3% in 8 years from Zeolite	No data.
	STATE OF DEVELOPMENT	Experiments still in progress.	Impregnated concrete - Advanced experimental. Organic compounds, hydrides - Experimental.	Zeolite - Advanced experimental. Ion implantation - experimental stage.	Well known.
	COST	\$356,000 in Ag for 600 kg I.	\$3.10-\$16.90 per gallon of tritiated water.		
CONTAINMENT PACKAGING	CANISTER CONTAINMENT TYPE			Pressure vessel containment. (for krypton gas)	55 gallon drums.
	CONTAINMENT LIFETIME			~500 years	
	STATE OF DEVELOPMENT			Well established	
	COST				40¢ a gallon

(1) 1500 MT/year reprocessing plant
(2) mixed with a comparable amount of I-127
(3) in the form of HTO
(4) CO_2

- Seabed disposal, which involves controlled emplacement in deep sea sediments or beneath the bedrock of the ocean floor. Crucial factors for selection of the repository are geological stability and the existence of deep sea sediments.

- Transmutation, which is feasible at the present time only in fission reactors. The neutron fluxes available and neutron cross-sections for these volatile nuclides are such that there is very little merit in this method. Fusion reactors, however, if eventually developed, may be capable of volatile nuclide transmutation due to their high neutron flux.

- Extraterrestrial disposal, where the long-lived nuclides are launched into space, so they escape the solar system. This is an expensive option and only C-14 and I-129 have lifetimes long enough to warrant the use of it. The amount of C-14 produced is of such low magnitude that it does not warrant such extreme measures. Iodine-129 alone should be considered as a serious candidate for space disposal, however, there is a serious concern regarding accidents during launching and possible reentry.

- Other continental disposal options such as mined cavities, a matrix of drilled holes, super-deep holes, deep well injection, and hydrofracture could have an application at appropriate locations where there are no major threats to long term containment through groundwater movement.

- Ice sheet disposal in Antarctica or Greenland, where thick ice formations are available, has been considered. Antarctica is subject to international agreements, and Denmark has sovereignty over Greenland. Apart from such political considerations, it is desirable to further investigate the evolutionary behavior and the effect of future climatic changes on the ice sheets.

- Storage for a period long enough to decay to non-hazardous levels could be a disposal option for tritium and krypton-85.

Feasible disposal options for the volatile radionuclides are shown in Table II. Data are insufficient on the physics and history of ice sheets for this concept to be considered practical.

Radiological health effects have not been considered in relation to alternative disposal methods.

TABLE II

SUMMARY OF VOLATILE RADIONUCLIDE DISPOSAL METHODS

	Iodine-129	Carbon-14	Krypton-85	Tritium
Geologic Disposal	Not likely to contain I-129 until sufficiently decayed. Would require identification of stable, water free, geologic formations with good iodine sorption capatility.	Appears to be a satisfactory disposal concept.	Appears to be satisfactory but may not be desirable to place Kr-85 with other waste in a repository. Engineered storage also possible.	Appears satisfactory but may not be desirable to place tritium with other waste. Engineered storage also possible.
Seabed Disposal	Not likely to contain I-129 until sufficiently decayed. Ocean dilution may reduce concentrations to acceptable levels.	Appears to be a satisfactory disposal concept.	Appears to be a satisfactory disposal concept.	Appears to be a satisfactory disposal concept.
Extraterrestrial Disposal	Satisfactory for elimination of I-129. Accident risk and consequences require careful study.	Probably not warranted because of cost and availability of other concepts.	Probably not warranted because of cost and availability of other disposal methods.	Probably not warranted because of cost and availability of other disposal methods.
Transmutation	Not a likely removal mechanism unless fusion reactors are developed.	Not a likely approach.	Not a likely approach.	Tritium could be used as fuel for fusion reactors if developed.

Iodine-129

The long half-life and generally low sorption characteristics of I-129 are such that it is difficult to assume that geological disposal will provide isolation of the waste for the period of time required for this radionuclide to decay to innocuous levels. The seabed is unlikely for providing complete containment but does provide an additional time barrier and ocean dilution prior to reaching biologically active areas to reduce the biological hazard.

Dilution of I-129 in the ocean following release from the seabed may reduce the concentration to acceptable levels. Slow release from containment is necessary to assure that local high concentrations do not occur.

Extraterrestrial disposal is attractive as a disposal option for I-129, however, the radiological impact of possible accidents must be carefully determined.

Transmutation of I-129 would only be feasible if fusion reactors were practical.

Carbon-14

Both geological and seabed disposal appear to be satisfactory concepts for the disposal of C-14. The cost of extraterrestrial disposal is not warranted if other disposal concepts are satisfactory.

Krypton-85

The disposal of Kr-85 in geological and seabed repositories appears to be a satisfactory option if it is separated from other

waste. Extraterrestrial disposal and transmutation are not required due to the relatively short half-life of Kr-85. In view of the short half-life, surface or underground engineered storage facilities could also be considered.

Tritium

Geological disposal and seabed disposal of tritium are both feasible and engineered storage may be more satisfactory. The tritium could be used as a fuel in the event fusion reactors were to become practical.

Extraterrestrial disposal of tritium does not appear to be a satisfactory disposal approach.

3.0 PROJECTED QUANTITIES AND COLLECTED WASTE FORMS

3.1 Introduction

Volatile radionuclides will be created in the process of nuclear electric power production. The bulk of these nuclides will be either released and collected at fuel reprocessing plants or contained and disposed of within the spent fuel in which they were formed. The volatile radionuclides may be packaged and disposed of in their collected form or further treated to reduce the potential for their release to the environment.

The quantities of volatile radionuclides produced will be affected by the installed nuclear electric power generation capacity. In a study that supported the EPA in developing environmental standards for high-level radioactive waste, presented projections of installed nuclear electric power were presented.[2] Projections estimated an installed gross nuclear electric power capacity in the range of 400 to 1000 GWe in the year 2010. A total commercial waste burden of spent fuel for the lifetime production of installed nuclear capacity up to the year 2010 was estimated in the range of 3.1-7.7 x 10^5 MTHM (400-1000 GWe). The estimated annual disposal requirements in the year 2000 for commercial spent fuel aged 10 years were 9.7-14.5 x 10^3 MTHM, based on a net installed nuclear capacity of 380 GWe to 570 GWe.

In this study, quantities of waste are referenced to a model spent fuel reprocessing plant assumed to be capable of handling 5 MT

per day (1500 MT/year) of spent fuel elements corresponding to 50 GWe years of nuclear power generation.[3] From 5 to 14 model reprocessing plants are required to handle 400 GWe to 1000 GWe of installed nuclear capacity, assuming a 70 percent capacity factor.

3.2 Iodine-129

Iodine-129 is produced in the nuclear fuel elements as a fission product and from the radioactive decay of other short-lived fission products such as Te-129, Sb-129, or Sn-129. I-129 decays to the stable isotope Xe-129, emitting beta and gamma radiations of 120 and 30 keV, respectively. The half-life of I-129 is 1.7×10^7 years.

3.2.1 Quantities Produced

The projected quantity of I-129 released from fuel in a 1500 MT/year model reprocessing plant is 380 kg/year.[4,5] This released I-129 has an activity of 66 Ci/year (approximately 1.3 Ci/GWe-year).* In addition, approximately 250 kg of stable I-127 are mixed with the I-129 in the off-gas steam. Thus a total of 600-650 kg of iodine per year has to be treated in the iodine removal system, immobilized, and disposed of for each model reprocessing plant. This corresponds to approximately 12-13 kg/GWe-year. One to five percent of the iodine may be present as organic iodine (methyl iodide CH_3I) in the effluent stream, or as HI and HOI.

*In contrast, the release from a typical LWR is negligible: 10^{-6} Ci/yr.[5]

3.2.2 I-129 Waste Form

The chemical waste form of I-129 depends on the technology utilized for collection. Four processes have been investigated for the collection of iodine: the Mercurex process, Iodox process, chemisorption process, and caustic scrubbing.[29]

The Mercurex process will yield 30 m^3 of liquid waste per year per model reprocessing plant. This is equivalent to 100 liters per day of 8 molar HNO_3 and 0.4 molar mercuric nitrate containing 1300 g of iodine in the form of mercuric iodide. Research and development are under way to convert the mercuric iodide to solid mercuric iodate or to barium iodate with recycling of the mercury. The purpose of this research is to convert the liquid to a solid waste, thereby reducing the waste volume and obtaining a less mobile waste form for further handling.

The Iodox process with nitric acid yields a very low solid waste volume (0.4 m^3/yr per model reprocessing plant) of nonvolatile mercuric iodate $Hg(IO3)_2$.

The chemisorption process yields 3.5 ton/year per model reprocessing plant, occupying 3 cubic meters and containing the 380 kg of I-129 in the form of chemisorbed silver iodide trapped in silver exchanged or silver impregnated adsorbents such as zeolite, silica, and alumina. The annual silver costs in this process are $356,000 for the total 600 kg of iodine captured. Other metals, such as lead, are being studied as exchange media to reduce costs.

Due to its very low efficiency of removal of organic iodine, caustic scrubbing is no longer being considered for collection of iodine from reprocessing plants.

3.3 Tritium

Tritium has a half-life of 12.2 years. It decays to stable helium-3 with the emission of a beta-particle with an energy of 18.6 keV. There is no gamma radiation.

Tritium production in light water reactor fuel is mainly by ternary fission--three fission products instead of the usual two, the third one being tritium. In addition, tritium can be formed by the (n,n alpha) reaction on Li-7 resulting from a (n, alpha) reaction of reactor neutrons on boron-10. Boron is present in control rods of most light water reactors and as a chemical additive in the reactor coolant of pressurized water reactors. PWRs usually use silver-cadmium-indium control rods but boron control rods have been used.

3.3.1 Quantities of Tritium Produced

Table III shows the annual production rate of tritium in a 1000 MWe LWR. The tritium produced in the control rods stays in situ until the end of the life of the reactor. The tritium produced in the reactor coolant of a PWR appears in the waste of the reactor coolant treatment system.

TABLE III

ANNUAL TRITIUM PRODUCTION IN A TYPICAL 1 GWe LIGHT WATER REACTOR

SOURCE ELEMENT	NUCLEAR REACTION	TRITIUM Ci/GWe yr	
Deuterium	Neutron capture	12	Reactor coolant
Uranium, plutonium	Ternary fission	25,000	Fuel rod
Lithium-7 resulting from neutron capture by Boron-10	(n, nα)	10,500	Boron control rods (BWR only)
Same as above	Same as above	1,100	Primary coolant (PWR only)

Source: Rhinehammer et al.,[6] p. 352.

The following discussion is limited to the tritium contained in the fuel elements treated at a reprocessing plant. The number of curies of tritium to be expected in the model reprocessing plant is 1.25×10^6 Ci per year.

There is considerable uncertainty regarding the chemical state and distribution ratios for tritium in the different pathways it can take at a fuel reprocessing plant. This is exemplified in Table IV, which gives ranges of estimates according to different sources for the various possible pathways. It is noted that the tritium fraction reclaimed in the cladding hulls after shearing can be high and depends on the burn-up of the fuel inside the cladding. Estimates on the dissolver operation off-gas also vary widely. The distribution ratios used by ERDA as a guideline in 1976 are indicated in Table V[2]. The total tritium is 30 percent lower than in Rhinehammer's evaluation given in Table III. In Table V, the tritium from the fuel cladding hulls is assumed to be recovered by wet processes in the form of tritiated water (HTO).

Table VI shows absolute maximum quantities of tritiated water that could be produced either in concentrated or in diluted tritium waste, and the volumes resulting in both categories. The ratio of the activities in concentrated or diluted categories vary according to the elimination process chosen.

TABLE IV

ESTIMATES OF TRITIUM DISTRIBUTION IN DIFFERENT PATHWAYS AT FUEL REPROCESSING PLANTS

PATHWAY	PERCENT OF TOTAL FISSION YIELD	FORM
Shearing operation off-gas	9.3[a]	Elemental
Tritium retained in the cladding hulls	14[b], 20[c], 47[d]	Elemental
Dissolver operation off-gas	1[b], 10[e], 20[f], 45[g]	Elemental, HTO
Uranium/plutonium bearing organic stream from solvent extraction process	1[e], 6[h], 20[h]	In combination with organic materials
Aqueous phase after solvent extraction process	Remainder	HTO

a) Zircaloy 2 cladding; burn up 43,000 MWD/MTHM, (Goode and Vaughen, 1970)[7]
b) ERDA 76-43
c) Zircaloy 2 cladding; 12,000 MWD/MTHM, (Grossman and Hegland, 1971)[8]
d) Zircaloy 2 cladding; 21,000 MWD/MTHM, (Grossman and Hegland, 1971)
e) Ribnikar and Pupezin[9]
f) Savannah River Laboratory
g) Musgrave[10]
h) Hall and Ward[11]

TABLE V

ERDA'S ESTIMATE OF TRITIUM IN FUEL REPROCESSING PLANTS

	PERCENT	Ci^3 H/MTHM	Ci/yr at 1500 MTHM/yr
Spent fuel input	100	547	820,500
Gaseous waste (as HT)	5	28	42,000
Cladding hulls	15	82	123,000
Dissolver solution (as HTO)	80	437	655,000
a) High-level waste concentrate	8	43	64,500
b) Low-level liquid waste	72	394	591,000
Comprehensively:			
As HT	5	28	42,000
As HTO	95	519	778,500

Source: ERDA 76-43, Vol. 1, p. 2.64., Reference 4.

TABLE VI

TRITIATED WATER PRODUCED BY A 5 MT/DAY REPROCESSING PLANT

SOURCE	CONCENTRATED TRITIUM WASTE	DILUTED TRITIUM WASTE
Liters/day	50 kg[3]	10^5 (10^5 kg)
Tritium Ci/liter	60	3×10^{-2}
Total Tritium Ci/day	3000	3000
Total Tritium Ci/yr[4]	900,000	900,000
Total Tritiated Volume		
Liters/year	15,000	3×10^7
m^3/year	15	3×10^4

[1]Condensate from head end process such as voloxidation.
[2]Condensate from evaporators and acid fractionators.
[3]Volume has not been determined, probably less than 100 liters/day.
[4]Assuming 300 operation days/year.

Source: ERDA 76-43, Vol. 2, p. 14.26., Reference 4.

3.3.2 Tritium Waste Form

There are three control systems for the collec-tion of tritium from reprocessing plants:

- Head-end process (voloxidation and pyrochemical techniques);
- Process-stream controls (recycle and/or isotopic separation);
- Retention of entire water effluent, including water removed from gas streams.

Voloxidation

The voloxidation process requires a front-end kiln to heat chopped fuel elements. Over 99 percent of the tritium becomes volatilized as tritiated water vapor (HTO) at temperatures ranging from 450 to 650°C. Off-gas from the chopper (where tritium is released as HT) is passed through an oxidizer to convert HT to HTO, which may then be removed by a drier-molecular sieve arrangement, trapping the HTO in a molecular sieve. Estimates of waste quantities from this process are less than 100 liters/day for a 5 MT/day reprocessing plant.

Pyrochemical Processing

In pyrochemical processing the cladding is selectively melted (stainless steel at 1450°C, zirconium at 1840°C) and the resulting bare fuel is reduced in a solution of zinc, calcium, magnesium, and calcium chloride at 800-900°C. During these steps, tritium is released as a gas together with the volatile radionuclides. Due to its small atomic size, tritium can be separated subsequently from the other gases. The complete process has not yet been demonstrated.

Process-Stream Treatment

In process-steam treatment, two techniques have been proposed to control the tritium once it has entered the aqueous streams of the reprocessing plant: water recycle and isotopic separation, expected to be used in conjunction. The most favored simple option (between total recycle without separation and no recycling, but direct separation of tritium from the effluent stream) is recycle with bleed stream separation to reduce the in-plant tritium concentration to a tolerable level. According to a study in 1975[11], in this option most of the tritium (94.5 percent) is removed as HTO vapor in the off-gas from the leacher (high activity side). Approximately 4.5 percent is removed from the low activity side in the form of tritiated waste containing tritiated water. The tritium removed in the off-gas in the high activity side for the model reprocessing plant amounts to 735,683 Ci/yr, and 3,500 Ci/yr are removed from the low activity side as liquid HTO.

Once recycle has been accomplished, isotopic separation can be more economically performed on the more concentrated bleeding stream. Six processes for isotopic separation are envisioned at present:

- Catalytic exchange (convert HTO to HT)
- Fractional distillation of water
- Distillation of hydrogen
- Electrolysis of water
- Reverse electrolysis (using a palladium diaphragm)
- Laser enrichment

The volume of tritiated water released from a recycle combined with a separation process (isotopic distillation) would be relatively small--on the order of 5 to 6 gallons per ton of uranium processed, i.e., 25 to 30 gpd or 7500 to 9000 gallons per year from a 1500 MT/year reprocessing plant.[12]

3.4 Krypton-85

Krypton-85 is the only long half-life noble gas radionuclide formed as a U-235 fission fragment that is present in appreciable quantities when the LWR spent fuel is reprocessed. The half-life of Kr-85 is 10.73 years and the major activity is beta radiation of 0.65, MeV followed by a gamma ray of energy 0.52 MeV. The krypton-85 gamma ray occurs in only 0.4 percent of the disintegrations. Krypton-85 decays to the stable isotope rubidium-85.

3.4.1 Quantities of Kr-85 Produced

The annual gaseous Kr production from a model reprocessing plant is about 530 kg, which has a volume of 143 m^3 at STP. About 6 percent of this krypton is Kr-85, for an aggregate radioactive discharge of 12.7 million curies.[13] This is equivalent to 254,000 curies per year for 1000 MWe of nuclear power generation.

Krypton gas is released during reprocessing at the chopper and dissolver steps. It is accompanied in the off-gas stream by xenon, unrecovered oxides of nitrogen, and air and water vapor. After treatment for nitric acid recovery and iodine removal, these off-gases pass through heaters (to avoid condensation), prefilters, and

high efficiency particulate air (HEPA) filters before further treatment of the purely gaseous components. It is at this stage that the krypton containing the radioactive Kr-85 at 6 percent concentration must be separated for further treatment. Krypton is only about .003 percent by volume of the total off-gas.

3.4.2 Krypton-85 Waste Form.

A number of methods are being developed in U.S. and foreign laboratories for the collection of krypton from off-gas streams. Each of these methods produces krypton in the gaseous state.

Cryogenic Distillation

The noble gases krypton and xenon may be separated from the off-gas stream by utilizing the widely separated boiling points of the main components.(14) At a pressure of one atmosphere, these boiling points are N_2O, -88,5°C; Xe, -108°C; Kr, -157°C; O_2, -183°C; and N_2, -196°C. The oxide N_2O deliquesces at room temperature and therefore must be removed before any temperature reduction to prevent solidification and blocking of the gas-flow lines in the system.

The process for cyrogenic distillation used at the Idaho Chemical Processing Plant (ICPP) and other U.S. installations is as follows. In addition to NO_2, water, O_2, and N_2O, are all removed prior to cooling since both N_2O and water will freeze. Oxygen is removed to minimize radiolytic ozone formation at cryogenic temperatures where the excessive oxygen concentration will pose a severe explosion hazard. Oxygen is catalytically recombined with

hydrogen to form water over palladium or platinum at 550°C. This step is followed by drying either by adsorption or freezeout. The N_2O is also removed catalytically at 370 to 600°C in a reaction which dissociates N_2O to elemental nitrogen and oxygen on rhodium. The rhodium is regenerated at 870°C under a reducing stream of hydrogen.[15]

The dried gas, which is a mixture of krypton, xenon, and nitrogen, is precooled to liquefy both xenon and krypton by countercurrent liquid nitrogen flow. Operating on a very reduced flow, the separation column fractionally distills the Xe-Kr mixture to yield mostly krypton at the top as 75 percent Kr, 25 percent Xe, and almost pure xenon at the bottom. Radioactive Kr-85 is confined to the krypton rich mixture which can be handled remotely and collected as a gas in pressurized cylinders.

At present, the Idaho Chemical Processing Plant (ICPP) system is operated intermittently as a pilot plant to validate and refine the technology for a full scale demonstration plant.[16]

Cryogenic Selective Adsorption - Desorption

A modification of cryogenic distillation has been proposed by a consortium in Japan.(17) This system consists primarily of alternate adsorption and desorption at reduced temperature and pressure. Experiments are presently underway to test the individual steps. It is planned that the system will eventually be used at BWRs on exhaust gases and at all other nuclear facilities. A major distinction from

the U.S. cyrogenic distillation process is that oxygen is not completely removed prior to cooling.

In this process, moisture and CO_2 are adsorbed on beds of synthetic zeolite. The concentration of noble gases is achieved on two adsorption beds of charcoal (A and B), using the following steps:

- Selective adsorption on A until a Kr concentration limit is reached at output;
- Desorption of A by evacuation at high temperature to pass noble-gas enriched flow to the next stage. Since the noble gases are not desorbed as easily as carrier gas, their concentration in the bed increases;
- Bed B is desorbed when bed A is adsorbing and vice versa.

The inlet flow to the storage system still contains nitrogen, oxygen, ozone, and some gaseous impurities. These are removed selectively by metal getters.

Fluorocarbon Absorption

Selective absorption of krypton by liquid fluorocarbon has been offered commercially in a process applicable for the off-gas from pressurized and boiling water reactors.[18,19] In the fuel element reprocessing, there are some additional problems in the krypton collection due to the presence of nitrogen oxides (NO, NO_2, N_2O), carbon dioxide, water, iodine, and methyl iodine. Recent ERDA results show that refrigerant-12 (dichlorodifluoromethane) demonstrated the most overall promise for selective absorption.[20] A fluorocarbon adsorption process designed for krypton removal can tolerate some impurities and be equally effective in the impurity removal--notably

iodine, methyl iodide, and C-14 in carbon dioxide. The process exploits the difference in solubility of the various gas constituents in the solvent and facilitates fractional distillation.

Other Collection Processes

Other collection processes are being developed for various types of reactor operations. At Oak Ridge National Laboratory (ORNL), adsorption in liquid CO_2 has been developed for the high temperature Gas reactor (HTGR).[21] In West Germany, a process has been developed for separating Kr and Xe from dissolver off-gas in reprocessing HTGR fuel. In the West German process, a helium purge-gas cycle is used for a coarse fractionation of krypton and xenon by cold-trapping at 80°K (-193°C). At this temperature, xenon is deposited in solid form at low pressures and krypton is deposited at 6 atmospheres. The separation by freezing is facilitated by the reduced partial pressure of the two gases with added helium.

Another krypton refraction process has been investigated at Westinghouse Electric Corporation for use with the liquid metal fast breeder reactor (LMFBR). Helium is being considered as a cover gas for this reactor and in the proposed process, charcoal would be used to adsorb krypton from the helium at temperatures between -140°C and -100°C. This process is very similar to the Japanese adsorption-desorption process.

3.5 Carbon-14

Carbon-14 is a low energy beta emitter with a half-life of 5730 years. It decays to the stable isotope nitrogen-14 with the emission

of a beta-ray with a maximum energy of 156 keV. Carbon, being a constituent of all organic materials, is easily absorbed into the biocycle.

In nuclear power reactors, C-14 is produced by (n,p) reaction with N-14 and (n,α) reaction with O-17. There is also a small probability of neutron capture in C-13. Oxygen-17 has a natural abundance of 0.037 percent and C-13 is 1.13 percent of naturally occurring carbon.

Carbon-14 is produced in both the fuel elements and in the cooling water in light water reactors. Nitrogen is present in the fuel interstices as an impurity and the amount present can vary over a wide range; twenty parts per million by weight is typical. Oxygen, of course, is a major component of oxide fuels used in LWRs. The reactor coolant of LWRs is also a source of carbon-14 where nitrogen is present as an impurity. Nitrogen is typically one part per million by weight in the reactor coolant water.

3.5.1 Quantities of C-14 Produced

Table VII lists the estimates of C-14 production in fuel elements and coolant water of both types of light-water reactors as published by Bonka et al.[22] and Kelly et al.[23]

Between 20 and 30 curies of carbon-14 are formed during the production of 1000 MWe-years of electric power. At the present time most of the C-14 produced in the fuel is released to the atmosphere as CO_2 during the dissolution of the spent fuel at the reprocessing

TABLE VII

CARBON-14 PRODUCTION IN LIGHT WATER REACTORS

(Ci/GWe-yr.)

		BWR		PWR	
		Bonka et al.	Kelley et al.	Bonka et al.	Kelley et al.
Fuel	^{17}O	8.4	2.7	7.1	2.7
	^{14}N	12.	10.9	12.2	10.9
		21.3	13.6	19.3	13.6
Coolant	^{17}O	9.9		9.8	
	^{14}N	1.3		1.3	
		11.2	16.0	11.1	6.0
TOTAL		32.5	29.6	30.4	19.6

plant. At the reactor site the isotope is released mostly in the gaseous form and the remainder is contained in the liquid waste. An average of approximately 17 Ci/year of C-14 is estimated to be produced in the spent fuel elements and 11 Ci/year is estimated to be released from the reactor per 1000 MWe-years of power generation. A model 1500 MT/year reprocessing plant would release about 850 Ci/year from the fuel.

The C-14 gaseous releases from light water reactors are not always in the chemical form CO_2. Based on various measurements,[24] it is estimated that the fraction appearing as CO_2 in BWRs varies between 66 and 95 percent. In contrast, over 90 percent of the gaseous C-14 activity in PWRs appear as CH_4 and C_2H_6, and only 10 percent as CO_2.[23] However, when the fuel elements are dissolved in nitric acid, the excess oxygen in solution from UO_2 and HNO_3 converts most of the carbon to CO or CO_2. Thus it is estimated that at least 95 to 99 percent of the C-14 contained in the fuel will be released to the off-gas system as CO_2.

3.5.2 Carbon-14 Waste Form

Methods for the collection of C-14 from off-gas streams include caustic scrubbing, molecular sieve adsorption, and fluorocarbon absorption. The most probable chemical form is calcium carbonate, which may be incorporated subsequently into concrete or other material.

Caustic Scrubbing

The obvious way to immobilize the carbon dioxide is by reacting it with a caustic to produce a carbonate. The most inexpensive such reagent is CaO (lime), however, the chemical reaction

$$CaO + CO_2 \rightarrow CaCO_3$$

is impractical because of the slow reaction rate. Two aqueous processes have been considered: (1) the direct reaction of CO_2 with a slurry of slaked lime $Ca(OH)_2$ where the fixation reaction is

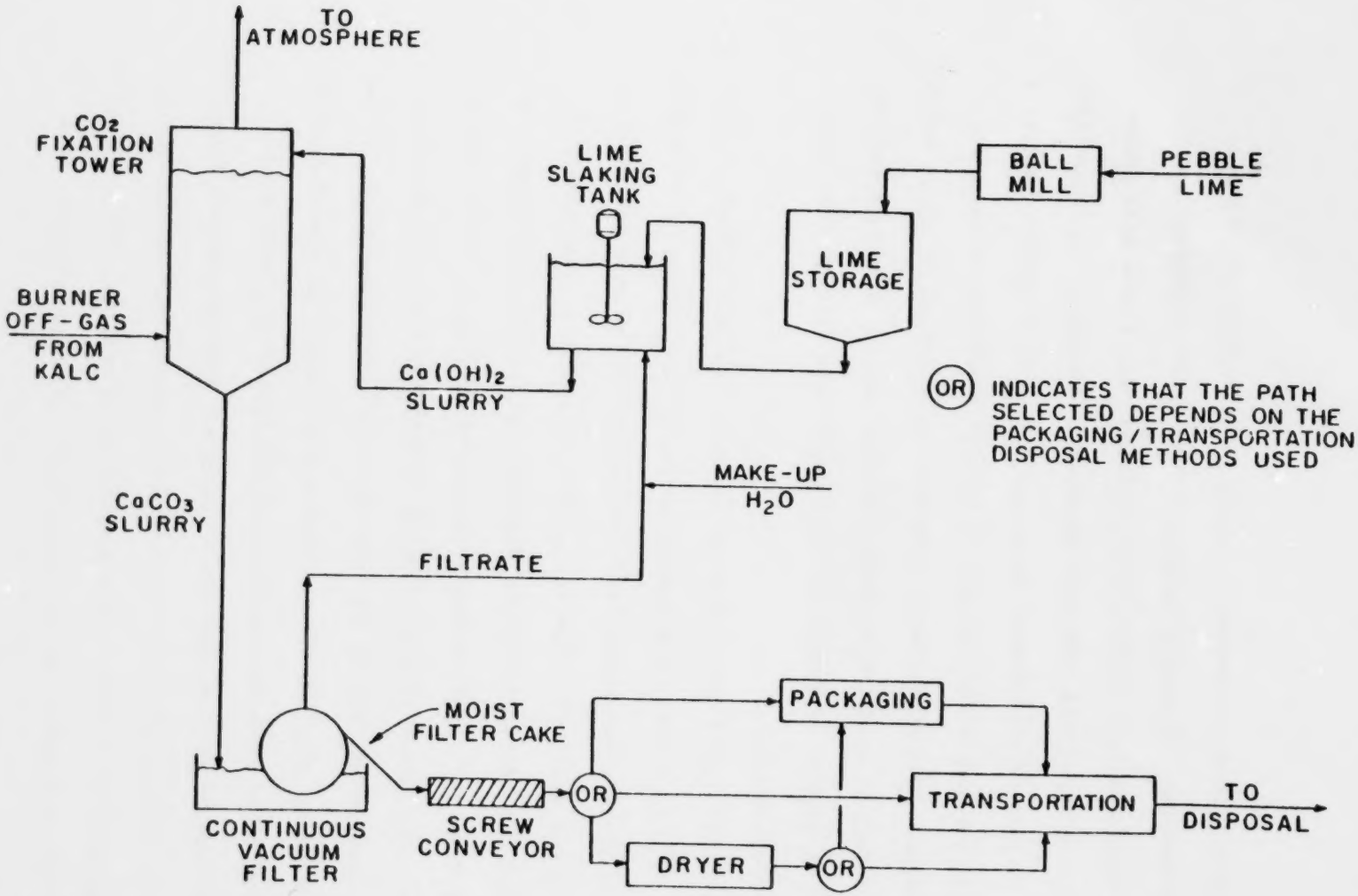
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

(2) the double alkali process which involves the reaction of CO_2 with NaOH to form Na_2CO_3

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

followed by the reaction: $Na_2CO_3 + Ca(CH)_2 \rightarrow 2NaOH + CaCO_3$.
It has been contended that the direct fixation is superior to the double alkali process on grounds of simplicity, smaller corrosion effects, and better economics.[24]

Figure 1 is a schematic of the direct fixation process. Pebble lime (CaO) is pulverized and slaked to produce the relatively insoluble $Ca(OH)_2$. The slaked lime is slurried and pumped to a fixation tower. CO_2 is bubbled through a sparger at the bottom of the tower and the gas combines with $Ca(OH)_2$ to produce $CaCO_3$, which also is insoluble in water. The slurry is filtered on a continuous filter and the filter cake is transported by screw conveyor a disposal system such as concretion.



Source: Croff, Reference 25.

FIGURE 1
SCHEMATIC OF THE DIRECT CO_2 FIXATION PROCESS

This process is assumed to remove 99 percent of the CO_2 initially present. It uses a relatively well known technology and is used industrially to produce $CaCO_3$ although very little mass transfer and reaction data have been gathered in the past. In industrial calcium carbonate production processes, there is a tendency to lose a significant portion of the product through leaky pump seals, pipes, and tanks. This situation is tolerable in an industrial plant because the product is relatively inexpensive, but careful attention must be given to quality assurance and maintenance when dealing with radioactive materials.

In the double alkali fixation process, the main difference is that NaOH is added to the make-up water; further, there is a reaction vessel wherein the sodium carbonate reacts with calcium hydroxide. The double alkali CO_2 fixation process is not used industrially because the calcium carbonate produced contains residual amounts of NaOH which should be removed by extensive washing to prevent corrosion. The only difference from the direct CO_2 fixation process is the presence of NaOH in the water used for slaking the lime. It has an advantage over the direct process with respect to availability of design data, since data on the reaction rate of CO_2 with aqueous NaOH, causticization, and lime slaking are available in the literature. Further, a CO_2 absorption tower contains only soluble sodium compounds, thus reducing the possibility of scaling. The presence of concentrated NaOH, however, could cause corrosion problems. The

capital costs of both systems are approximately equal. The operating costs are also expected to be about the same except for the additional sodium hydroxide needed. Assuming 99 percent recovery of an average of Ci of $^{14}CO_2$/year, the average annual output of radioactive calcium carbonate is about 1.36 kg. However, ten to 100 times as much $CaCO_3$ from atmospheric carbon dioxide would probably be recovered along with C-14 species.

Molecular Sieve Adsorption and Fluorocarbon Absorption

In addition to fixation in $CaCO_3$, two other methods have been evaluated: molecular sieve adsorption and fluorocarbon absorption. In the former, the carbon dioxide is removed by adsorption on a molecular sieve. Impurities such as N_2O, NO, NO_2, and water vapor must be removed. N_2O is removed by catalytic decomposition using rhodium as the catalyst. NO and NO_2 are removed as nitric acid. The resultant gas is dried on a 3A molecular sieve and the CO_2 is adsorbed on a 5A molecular sieve.

To collect the carbon, the molecular sieve is regenerated by heating in a gas purge, and the regenerated gas is scrubbed to produce $CaCO_3$. The technology for this process is not fully developed at this time.

Fluorocarbon absorption utilizes the solubility of carbon dioxide in fluorocarbons. It has been developed on a pilot plant scale at Oak Ridge, but has not been demonstrated on actual dissolver off-gas.

4.0 IMMOBILIZATION TECHNOLOGY

Various methods can be utilized to isolate the volatile radionuclides from the biosphere. The methods for imposing barriers to the transport of these nuclides into the environment fall into four general categories of engineered isolation:

- selection of the chemical waste form
- immobilization in a solid matrix
- outer containment (packaging)
- structural or natural barriers at storage or disposal sites

It is desirable that the highly mobile volatile nuclides be converted to a physically and chemically stable nonvolatile, nonsoluble compound where possible. Various chemical compounds are under consideration for I-129, C-14, and tritium. However, the noble gas krypton does not combine into a stable physical compound at normal temperatures and pressures and other forms of immobilization are required. Krypton and the chemical compounds of the other radionuclides can be incorporated into a solid matrix thus providing an immobilization barrier and delaying their release into the environment. The solid matrix material selected must be capable of withstanding the nuclear radiation and high temperatures that may result from radioactive decay heat. The release of the nuclides under consideration can be further restricted by using an outer packaging, e.g., metal containers both to contain the radioactive nuclides and to resist and delay the effects of corrosion, erosion, and leaching which could eventually release the

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radioactive elements. Finally, the storage or disposal method or site can be engineered or selected in such a way that if the nuclides escape the packaged containment, there will be secondary containment, i.e., the transport into the biosphere will be sufficiently delayed so as to allow natural radioactive decay to reduce the biological hazard. An additional safety factor can be obtained by selecting the storage or disposal site such that releases into the environment are diluted prior to reaching areas of human exposure (e.g., atmospheric dispersion or dilution in the sea in the case of seabed disposal).

This section discusses chemical waste form, immobilization technologies, and research that has been conducted to measure the leach rate from different immobilization forms of the radionuclides. Containment packaging is also briefly addressed. Alternatives for the storage and disposal of the volatile radionuclide wastes are included in Section 5.0.

4.1 Iodine-129

Features of Iodine-129 which present particular problems in the waste management of this radionuclide are as follows:

- A long half-life (16 million years) such that complete isolation from the biosphere until quantities of this radioisotope decays to innocuous levels cannot be assured;
- The iodine compounds are not stable at temperatures above a few hundred degrees, thus incorporation into glass matrices as proposed for other radioactive waste is not practical;
- Most iodine compounds are soluble to some extent in water;

- Iodine ion exchange with most soils is not as favorable as that of other elements.

The radioactive iodine can be chemically combined into several iodide and iodate compounds. Table VIII gives the solubility of these various iodine compounds. Among the iodates, the mercurous salt is the most insoluble (1.1-1.6 x 10^{-12} kg mole/liter) but the few preliminary experiments with the mercurous salt have not been successful in obtaining lower leach rates than with the barium iodate[25]. Barium iodate is particularly favored for incorporation in concrete. The chemisorption of iodine on silver and lead exchanged zeolites, forming the silver and lead iodides, has also been investigated.

The inclusion of any compound of radio-iodine in glass does not appear feasible because iodine compounds dissociate at the temperature where glass melts. Various researchers state that I-129 cannot be easily immobilized in glass matrices and that no development work is currently in progress.[26,27,28] There is a possibility of introducing iodine into glass by use of a pressurized system, but this is not considered practical at present.

4.1.1 Immobilization of Iodine

Barium Iodate in Concrete

Barium iodate has been investigated for immobilization of iodine in concrete for three reasons:[29,30] 1) its low solubility (8.1 x 10^{-7} kg-mole/liter at 25°C); (2) it can be prepared directly from partially soluble barium hydroxide without using any superfluous

TABLE VIII

SOLUBILITIES OF SELECTED IODINE COMPOUNDS IN WATER*

	Solubilities[a] (10^{-3} kg-mole/ at 298°K)[b]	
Cation	Iodide	Iodate
Sodium	8.2	0.47
Potassium	4.7	0.42
Magnesium	5 molal[c]	0.25
Calcium	4.9 at 20°C	7.9×10^{-3}
Barium	4.0	8.1×10^{-4}
Lead	1.65×10^{-3}	$(3.6 \text{ to } 5.5) \times 10^{-5}$
Silver	1.1×10^{-8}	1.8×10^{-4}
Mercuric	9.7×10^{-5} to 1.3×10^{-4}	"Insoluble"[d]
Mercurous	3×10^{-10} (Hg_2I)	$(1.1 \text{ to } 1.6) \times 10^{-9}$ ($HgIO_3$)

*The cations selected include those most abundant in Portland cement (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, omitting Al^{3+}, Fe^{3+}, and Si^{4+} and those that form the most insoluble, simple compounds of iodine (Ba^{2+}, Ag^{+}, Pb^{2+}, Hg^{2+}, and Hg_2^{2+}).

[a]Molar solubilities were calculated from data obtained from A. Seidell, W.F. Linke, Solubilities of Inorganic and Metallorganic Compounds, 4th ed., American Chemical Society, 1958, as indicated.

[b]Except where indicated.

[c]Lack of solution density data prevented conversion to molarity.

[d]From N.A. Lange, Handbook of Chemistry, revised 10th ed., pp 278 -279, McGraw Hill, New York, 1967.

ion species and all of the resulting slurry of barium iodate can be incorporated in the concrete product so that no liquid waste; and (3) the iodate form is compatible with the Iodox process, which is under development at ORNL for collecting the I-129 waste. This process yields essentially 100 percent iodic acid HIO_3 from which barium iodate can easily be prepared.

It has been found that approximately 10 weight percent iodine in the form of barium iodate can be incorporated into concrete. It is estimated that the fission product iodine, after decay of the short-lived iodine isotopes, will consist of 75 percent I-129, the remainder being I-127. In this form, the heat generation amounts to 3.6 microwatt/kg of concrete. This heat generation is considered negligible for all practical purposes and cannot give rise to temperatures which would impair the long term stability of the iodine compounds in the concrete.

Approximately 6000 kg of concrete of volume 2.6 cubic meters is required for the disposal of 600 kg of iodine from a model reprocessing plant.

Iodine Leaching from Concrete

It appears that the rate at which water penetrates concrete is slow, so only a small fraction of the radioiodine compound is in contact with water at a given time at the solid/liquid interface inside the concrete. This effect slows down the dissolution rate of the radioiodine.

The solubility of a chemical compound is not related in a simple way to the concentration of this compound in water when the compound is embedded in concrete. Tests in stagnant water must be made to find the upper limit of concentration of the compound in water. When the water is flowing or changed at regular intervals, the conditions are different from those with stagnant water.

For barium iodate incorporated in concrete, some leach tests have been conducted under dynamic conditions simulated by changes of leachant at regular intervals.

Small, but finite, leach rates were measured by Clark and Moore on concrete cylinders 50 mm x 50 mm, including up to 11.9 weight percent iodine.[26,29]

In one experiment, the leachant (distilled water) was changed every day at the beginning, every week later on, and every month at the end of the test period.[29]

The cumulative leach rates obtained are shown in Figure 2. The ordinate is the function

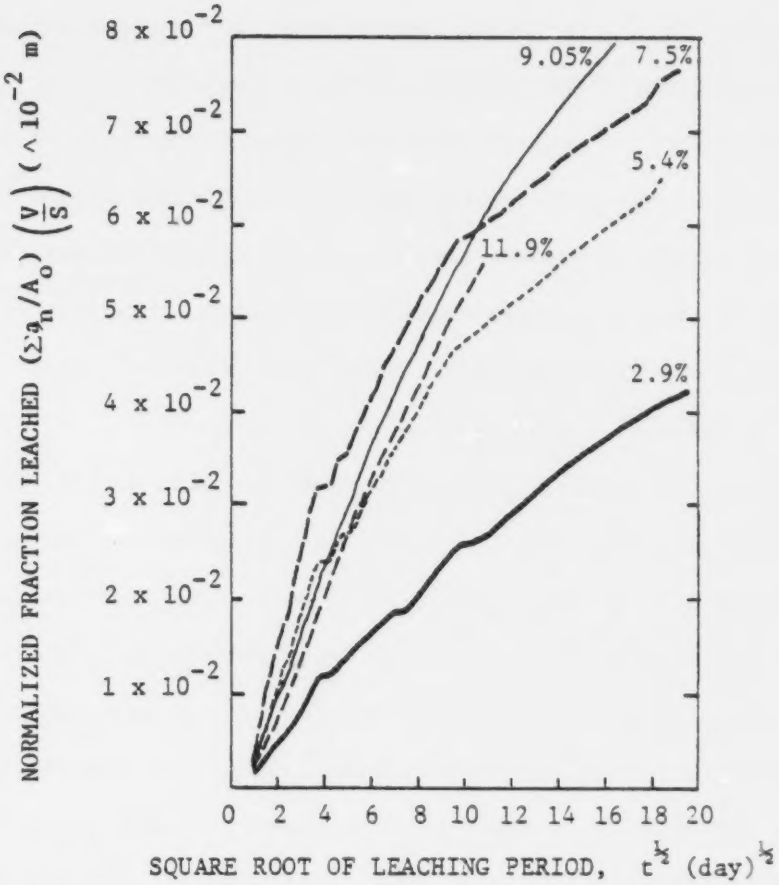
$$\sum_{n}(a_n/A_o)\ (V/S)$$

where a_n is the weight of iodine leached per leaching period;

A_o is the initial iodine content of the specimen;

V is the specimen volume;

S is the apparent specimen area.



SOURCE: W. E. Clark, 1977, Reference 29.

FIGURE 2
THE EFFECT OF IODINE CONTENT ON THE LEACH RATE OF BARIUM IODATE CONCRETE, NO ADDITIVES

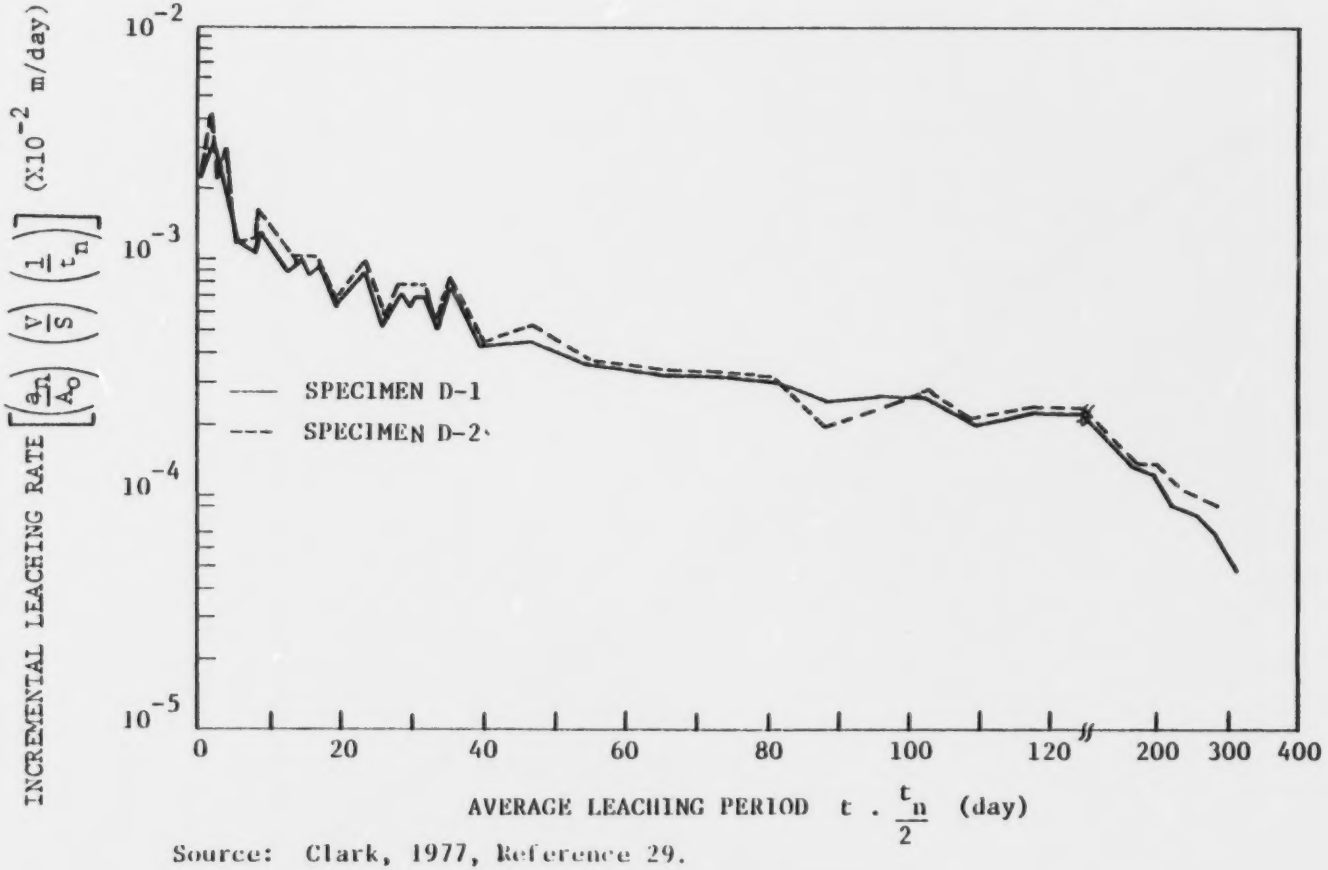
This function is plotted versus the square root of the total leaching period for various iodine contents in weight percent in the concrete. The leach rates in this experiment were found to decrease with time (Figure 3), and the leach curves (Figure 2) exhibited a bend toward a saturation effect. When the experiments were repeated, was changed every day.[29] Moore repeated Clark's experiments, this time changing the leachant every day. This curve (Figure 4) shows no saturation effect.

Figure 4 can be extrapolated to determine when all of the radioiodine will leach out of a concrete block. While not appropriate in the practical case for reasons noted below, the exercise is of interest in indicating the difficulties of containing I-129 for the periods required for the radioactivity to decay to innocuous levels.

The 600 kg yearly output of iodine from a model reprocessing plant can be mixed with cement to form 6000 kg of concrete. This quantity is assumed to be cast into a cubic block. Assuming a density of 2.3 grams/cm^3, a side of the cube would be 140 cm and the volume to surface ratio a/b = 23 cm. Assuming a linear relationship i Figure 4.

$$\sqrt{t} = (23)\left(\frac{14}{0.13}\right)_2$$

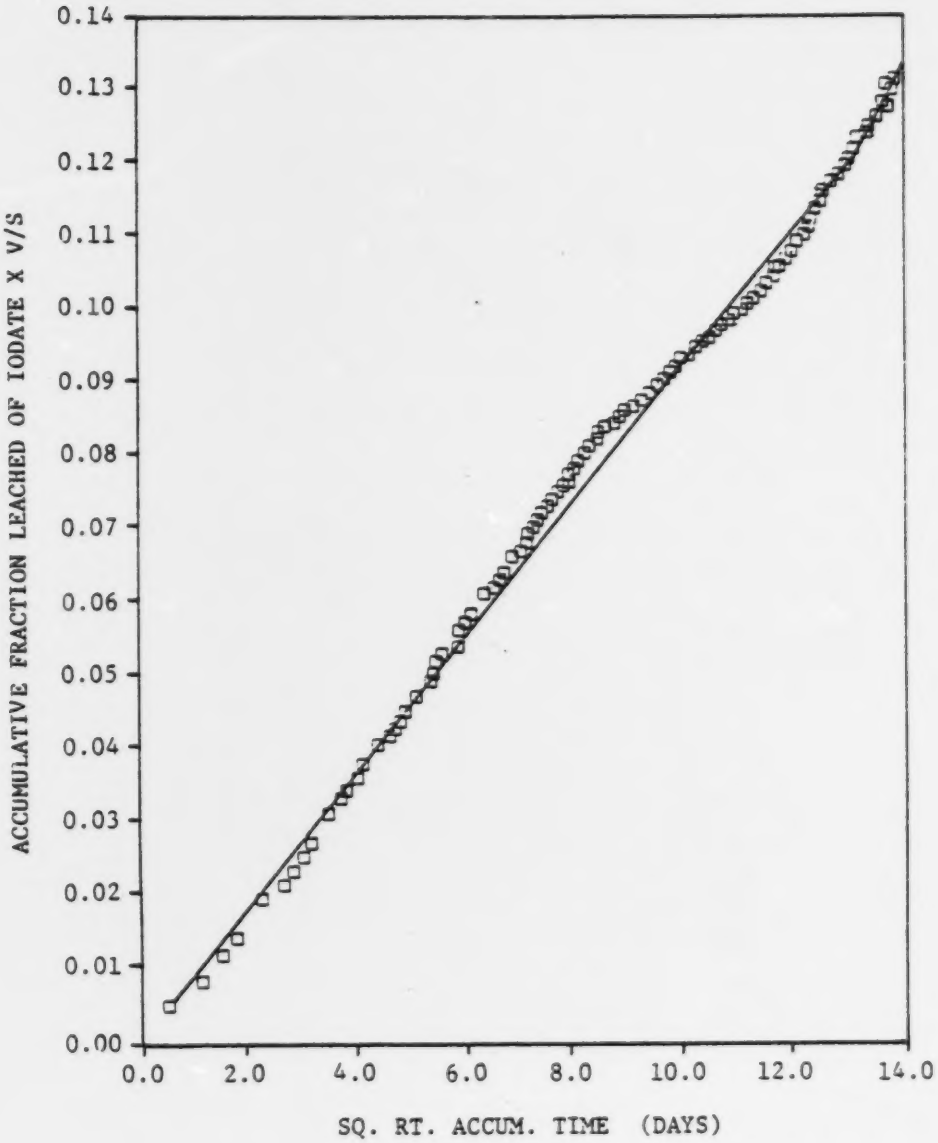
or $t = 6.13 \times 10^6$ days $= 1.68 \times 10^4$ years. This time period is insignificant compared to the half-life of I-129 (1.7×10^7 years) i.e., nearly all of the I-129 would exist at the time of complete leaching from the concrete block.



Source: Clark, 1977, Reference 29.

(t_n is the time period between changes of leachant)

FIGURE 3
INCREMENTAL LEACH RATE OF BARIUM IODATE FROM CONCRETE CONTAINING 9.5 WT% IODINE



Source: Moore, 1977, Reference 26.

FIGURE 4
LEACHABILITY OF IODINE INTO CO_2 FREE DISTILLED WATER FROM TYPE I PORTLAND CEMENT CONTAINING 9.55 WT% IODINE AS BARIUM IODATE (WATER/CEMENT RATIO = 0.89; CURED 56 DAYS)

This example is not a good representation of what is likely to occur in the practical case. Reasons for the inadequate representation are discussed below.

First, the leach test that was conducted extended over a period of a few hundred days, during which the cumulative leached fraction increased linearly with the square root of time. Other effects, such as those due to the penetration of the leachate in concrete, or the diffusing of the iodine, are not yet apparent. Concrete dams are known to hold water and recent Japanese work has shown that it takes one year for sea water to penetrate 1 centimeter deep into a concrete block.[31] Obviously, the leaching experiments did not extend over a time period sufficient to penetrate the 5 cm height x 5 cm diameter samples that were used. Further studies are necessary to define the long term leach rate of iodine from concrete in order to arrive at meaningful conclusions.

Second, the leachate used in laboratory tests was distilled water. Tests are currently in progress with leachates comparable to those that are found in nature, using salt water, brines with various concentrations of minerals and well water.[32] These tests show that the leach rates are much smaller than with distilled water.

Third, there are doubts on the inverse dependence of the leach rate on the volume to surface ratio. It is deemed possible that this dependence breaks down at small volume to surface ratio, due to depth of penetration effects.

Fourth, the leaching process is different in stagnant or flowing waters. The influence of the flow speed of the leachant has to be considered.

It is not inappropriate to conclude that current leach rate data cannot be used to adequately predict I-129 concentrations in ground water streams leaching the concrete blocks. Much work is necessary to define the various physical phenomena involved in the leach process. However, there are inherent difficulties and uncertainties of projecting leaching or any other effects extending over time periods comparable to the half-life of I-129. Accordingly, the pursuit of further research must be weighed against the benefits to be derived. It is recommended that the methods of immobilization of I-129 be considered only as an interim means of containment and not by themselves as a form of isolation of this radionuclide from the biosphere.

4.1.2 Immobilization of Iodine in Zeolite

As noted in section 3, zeolites can be used to separate iodine from the waste. The zeolites can also be used to immobilize iodine collected by other processes.

Silver-exchanged zeolites were found to have a high chemisorption capacity for elemental iodine in gaseous streams.[32] The maximum iodine chemisorption capacity of silver zeolite at 150°C was found to be 214 mg of iodine per gram of zeolite, based on a dry bed density of 0.85 g/cm^3. This is 60 percent of the stoichiometric capacity

based on the number of silver sites per gram. Because silver is a valuable commodity, tests on desorption of iodine from the silver for recycling used silver beds and of chemisorption of iodine on lead exchanged zeolites have been performed.[33,34] In this latter process, it appears that a compound with a chemical formula approaching PbI_2 is formed, which is then chemisorbed in the zeolite and is stable at 150°C and remains kinetically stable once cooled to room temperature in the presence of air. A loading of 317 mg. I_2/g of lead exchanged zeolite (PbX) is possible and represents 88 percent of the stoichiometric capacity based on the number of lead sites per gram.

The annual disposal of 600kg of iodine per model reprocessing plant would require about 1900 kg or 2.2 cubic meters of zeolite per year.

The zeolites proposed for use for both silver and lead are silica mixed with alumina with a silica/alumina ratio of 5 to 1. As an example, when combined with PbI_2, 40 percent of the resulting weight is PbI_2.

No research on the leaching of iodine from zeolites was identified in this study. It is noted, however, that current tests to fix iodine in zeolite are made with X-type zeolite.[33] This zeolite is not acid resistant. Since ground water streams are often acidic, it would appear desirable to investigate the Z-type zeolite (Zeolon) which resists attack by acids. The zeolite could be utilized as the

waste form for the disposal of I-129, or zeolites could be mixed with cement to form a concrete. Zeolite usually appears in the form of 10/20 mesh granules, i.e., they have an average diameter of about 2mm. These granules have a crystalline structure, are hard, and are expected to mix readily with cement. The casting of the iodine containing zeolites in concrete may provide a worthwhile additional barrier to the transport of iodine. However, experiments to investigate this method of containment do not appear to have been made to date.

No leach tests are available on iodine loaded zeolite incorporated in concrete. It is estimated, however, that the solubility of lead iodide (PbI_2) and silver iodide (AgI), when adsorbed on zeolite, is about one half of the solubility of these salts when pure.[35] Research to investigate the immobilization of iodine loaded zeolite in concrete and tests on the leachability of the iodine compound from the concrete matrix may be desirable in developing an improved waste form.

4.2 Tritium

In principle, there is a choice between chemical storage and containment. In chemical storage, a hydrogen-containing compound is utilized as a solid storage medium. In containment, tritiated water is stored in its unaltered form.

Chemical storage technologies include the use of polymer impregnated hydrates (such as drying agents or hydraulic cements), organic compounds (such as polyacetylene, bakelite analog polymers,

polyacrylonitrile, polystyrene) and hydrides (especially zirconium and titanium hydrides). Characteristics of these compounds are presented in Table IX.

Containment can be accomplished by utilizing high-pressure steel cylinders or large above-ground storage tanks. The storage can be either interim storage for low level waste (it takes 100 years for 10^{-3} Ci/liter water to decrease to the maximum permissible concentration (MPC) in water of 3×10^{-9} Ci/ml) or final storage for high-level concentrated waste. Table X shows the properties of contained storage options. Table XI gives a summary of current storage practices.

4.2.1 Polymer Impregnated Tritiated Concrete (PITC)

Leaching of Tritium from Concrete

Leaching tests have been conducted at the Savannah River Plant Plant on PITC prepared at Brookhaven National Laboratory.[36] The block was lowered into the ground and leached by rain water. Leach rates obtained were less than those obtained in static leaching when the block was fully immersed in distilled water. To be conservative, the results of the static leaching test (which was more severe) will be cited, as these results are more applicable to concrete immersed in a continuously flowing stream of water. Figure 5 shows the tritium release as a function of time and the same curve corrected for decay. The release rate is:

$$\sum_n \frac{a_n}{A} \left(\frac{V}{S}\right) \left(\frac{1}{t_n}\right) = 8.61 \cdot 10^{-5} \text{ cm/day}$$

TABLE IX

CHARACTERISTICS OF CHEMICAL STORAGE TECHNOLOGIES FOR TRITIATED WATER

	Water Loading wt %	Tritium Release Rate	Remarks	Availability of Technology	Radiation Resistance G(liberated molecules/100 eV)
1. Hydrates					
a) Drying agents					
Calcium sulfate	6.2			Available for removing HTO vapor	
Silica gel	40	10^{-3}-10^{-4}/day	Low cost Only at low loadings		
Activated alumina	20			Encapsulation in concrete and polymers also available	
Molecular sieves	10-20	10^{-3}-10^{-4}/day when encapsulated in polystyrene	Stable with respect to heating, water, various chemicals	Polymer impregnation requires development	
b) Hydraulic Cements					
Portland cement	25	10^{-2}/day (first month) 2.5×10^{-3}/day (when asphalt coated) 3×10^{-4}/day (when 1" asphalt cast around) 10^{-4}/day when polymer impregnated (5-15 wt%)		Available, coatings available; polymer impregnation requires development	
2. Organic Compounds					
Polyacetylene	Hydrogen from 0.68g of water can be incorporated to 1g of polyacetylene	4% initial, none further	Thermally stable to 325°C; insoluble in all solvents	Available	0.15
Bakelite analog polymers		2% loss in rinsing, none further	Stable to 230°C; insoluble in various solvents	Acetaldehyde production available, polymerization also requires improvement	0.08
Polyacrylonitrile	Hydrogen from 0.18g of water can be fixed in 1g of polyacrylonitrile	5% in initial rinsing	Thermal condensation above 200°C; degraded by alkali	Available. Purification necessary, complex, expensive	0.39 (total gas); 0.1 (hydrogen)
Polystyrene	0.5g of water per g of polymer	Not measurable	Degradation above 280°C	Available; problems in tritium-control	0.03 - 0.02
3. Hydrides					
Zirconium, $ZrH_{1.4}$	1.5 wt% H (0.14g of tritiated water)	5×10^{-4}/year in NaOH 4×10^{-5}/year in dist. H_2O 2×10^{-4}/year in HCl	Stable below 300°C Zirconium sponge 5.50-13.00 $/lb in 1970	Available; development of facility able to fix 50 Kg HTO/day requires 4 years	
Titanium			Stable below 300°C		
Uranium, UH_3					

Source: ERDA 76-43, Vol. 2

TABLE X

PROPERTIES OF ENGINEERED STORAGE OPTIONS FOR TRITIATED WATER

	VOLUME LITERS	LIFE TIME YEARS	REMARKS	AVAILABILITY	POSSIBLE ACCIDENTS	PRECAUTIONS
High Pressure Steel Cylinders						
Type IH (for high level concentrated waste	18		Corrosion to be evaluated.	Available, corrosion control required.	Corrosion, material fatigue	Temperature control, monitoring, chemical pH adjustment
Above Ground Storage Tanks (for low level diluted waste)	1.2×10^7	>40	Carbon steel construction, protection from ice formation by insulation and tank heaters; can be an interim procedure.	Available, corrosion control by pH adjustment	Radiolysis producing hydrogen, oxygen and recombination Leakage Sudden rupture	Monitoring, catalyst to promote recombination reaction Pumping to reserve tank Double containment, transfer lines Secondary containment

Source: ERDA 76-43, Vo. 2

TABLE XI

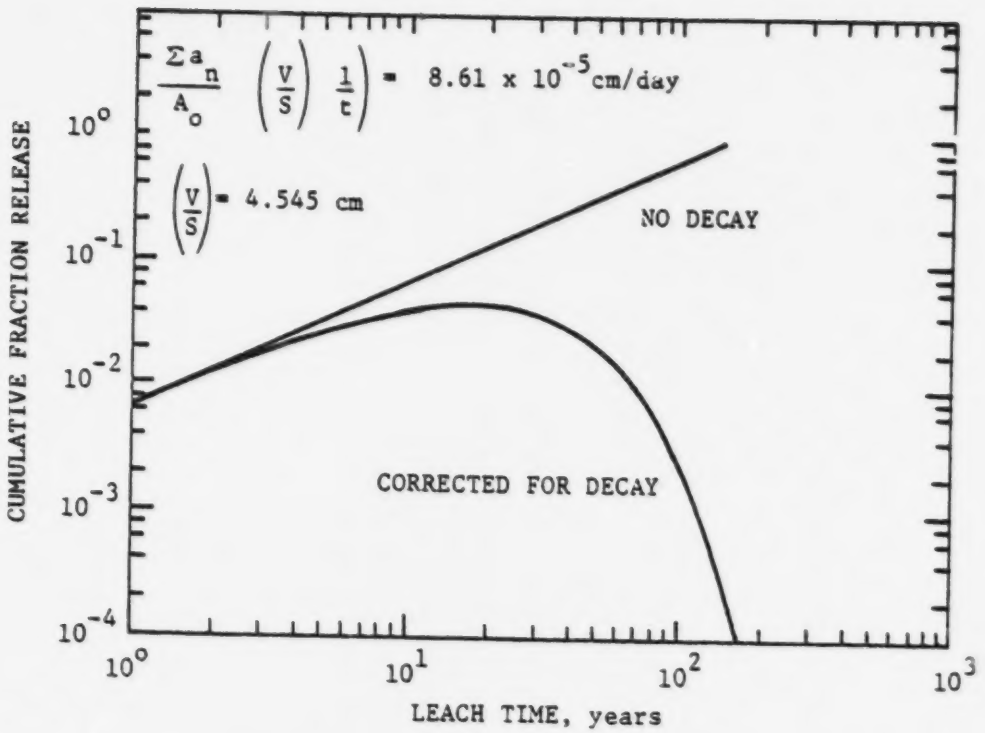
SUMMARY OF CONTRACTOR STORAGE PRACTICES

Form	Container Disposal Method
Solid	
Uranium titride	SS containers with valves
Tritiated materials and wastes " " " " (long term storage)	Double O-ring sealed anodized aluminum continers Welded SS cylindrical continers
High level (>200 Ci/drum to >1000 Ci/drum)	≥20,000 Ci HTO absorbed on 2 kg dessicant in sealed metal cans and concrete and ≥50,000 CiHTO in welded 5" x 11" SS vessels coated with asphalt and packaged with vermiculite in an asphalt coated 30 gallon 17H drum
Intermediate <1000 Ci drum	Sources cast in plastic, molecular sieves in 6" diameter aluminum condult
Low level <10Ci/drum <10Ci/ft^3	Plastic bags, cardboard boxes, drums burial in ground
Liquid	
High level >100 Ci/drum >10 Ci/liter (Vacuum pump oils), water from inert gas purification systems)	Collection of HTO on absorbent, packaging in plastic bags and cand for burial, or solidification of HTO >1000 Ci/liter on adsorbent or with plaster-cement mixture in polyethylene containers inserted in 30 gal. metal drum, and filled with asphalt
Intermediate and low >1 Ci/liter; >40 Ci/liter	Solidification with cement, absorption on vermiculite, all in metal drums. Absorption on absrobents. Disposal of contaminated objects such as pumps, in asphalt lined concrete filled drums. Solidification of low level (0.1 Ci/liter) on pelletized corn cobs collected in polyethylene lined streel drums for burial

TABLE XI (Concluded)

Form	Container Disposal Method
Gaseous	
	Converted to HTO for absorption on drying agent and disposal as a solid
	Discharge of low level waste gases (<0.01% ^{3}H) through zeolite to collect HTO before exhaust
	Tritium oxidation and collection on zeolite or molecular sieve beds
	Elemental tritum: SS tanks at pressure <2 atm

Source: Rinehammer, 1973, pp. 329-336



Source: Colombo (1976), Reference 36.

FIGURE 5
PROJECTED TRITIUM RELEASE VERSUS TIME FOR STATIC LEACHING OF THE SRL LYSIMETER TESTING DUPLICATE SPECIMEN (WITHOUT CONTAINER) IN DISTILLED WATER

with the same definitions as in section 4.1. The specimen volume to surface ratio is 4.545 cm. Total release of tritium from the specimen is estimated to be complete after 145 years. The maximum activity present in the environment occurs after 17.7 years and is equal to 4.45 percent of the initial tritium activity fixed in the block when the immersion in water is accomplished.

The costs of high-level tritiated waste fixation in PITC have been estimated.[37] A hypothetical installation disposing of 1200 liters/yr of high-level tritiated water in PITC has been estimated to have operating costs of $6,327/yr including containers, formulation polymerization, labor, freight, burial, and handling. This amounts to $5.27/liter of tritiated water. Capital costs have not been estimated. The major parts of the facility include a tritium storage and filling station, a drum tumbling station, a monomer storage and filling station, a water bath curing station (if required), a drum filling station, a transport cart with load cell, and an overhead crane, which is normal equipment in the chemical and building industries.

Monsanto Tritiated Liquid Waste Packaging

An improved method for packaging tritiated liquids for burial was developed at Monsanto Mound Laboratory.[38] The burial package is prepared by inserting a 27-gal polyethylene drum into an asphalt-coated 30-gal steel drum. The polyethylene drum is filled with either 81 kg (90 liters) of a 3 to 1 dry mixture of plaster and cement

for tritiated water waste, or 9.5 kg (90 liters) of vermiculite or absorbal for organic wastes (pump oils). A recommended maximum of 35 liters of tritiated water (or 28 liters of tritium contaminated pump oils) can be enclosed. The polyethylene drum is sealed and the void volume above it is filled with asphalt. The steel drum lid is then sealed in place using a sealant and a bolted clamp ring.

These packages were tested in running water to determine the tritium permeation rate. Based on the test results, it is concluded that the amount of tritium released from the package to the ground water each year would not exceed 0.0001 percent of the total tritium contained in the package. Since there is a 5.5 percent natural decay each year, the projected maximum tritium released during 85 years of burial would be 0.002 percent of the total tritium in the package, or 1.6 Ci from the 70,000 Ci (recommended maximum) package.

4.2.2 Organic Compounds

Methods for industrially fixing tritium in bakelite (resorcinol or phenol acetaldehyde formaldehyde), polyacrylonitrile, and polystyrene have been studied.[39] Leaching tests (Table XII) show initial release of tritium of the order of a few percent during rinsing, except for polystyrene. No further loss was detectable over a 4 to 6 week period of testing (the sensitivity of the measuring equipment was not indicated). Although this shows the organic compounds route is promising in this respect, more extended tests with large samples should be conducted.

TABLE XII

LEACHING DATA OF POLYMERS

Polymer	^3H Content of Polymer(a)	Total ^3H Content Exposed per ml Rinse Solution	% Total ^3H Content Lost During Rinse(b)	% ^3H Leached Following Initial Rinse(c)
Bakelite	2874 d $min^{-1}g^{-1}$	1430 d min^{-1}	2	0
Poly (acrylonitrile)	7650 d $min^{-1}g^{-1}$	5130 d min^{-1}	5	0
Hydrogenated Polystyrene	690 d $min^{-1}g^{-1}$	794 d min^{-1}	0	0
Polyureylene/polymethane	---	---	3	3(c)
Polystyrene Tritiated on Rh/Al_2O3	---	---	0	0

(a) Determined from combustion analysis of polymer and scintillation counting of resulting water.

(b) Determined by scintillation counting of rinse water.

(c) Only during first three days, none thereafter.

Source: Franz and Burger (1975,1976).[39,41]

Unfortunately, more recent work reports difficulties in developing tritiated bakelite and acrylonitrile;[41] therefore, two new methods of preparing polymeric media were investigated. One method uses polyurethane/polymethane copolymer, which gives a loss of 6 percent of activity in rinsing with no further release 3 days thereafter. The second method tritiates polystyrene with a rhodium-on-alumina catalyst, which offers a one-step fixation procedure. The resulting material is inert to exchange of hydrogen and is already in a polymeric form for storage.

Material costs have been estimated for polymeric media by the and are shown in Table XIII. The estimated cost of isotope separation of tritium is also included in the table. Polyacetylene costs have been estimated by Colombo[42] (based on laboratory experiments) and the polymer impregnated concrete costs are more recent estimates.[37] Deep well injection costs are estimated [43] as well as long term tank storage and isotope separation costs. [44] There are no process cost estimates.

4.2.3 Hydrides

At Battelle, zirconium hydride has been investigated as a storage medium for tritium.[45] Conditions of preparation have been developed such that hydrogen to zirconium ratios in the range of 1.5 to 2 are obtained. Pure hydrogen gas at 760 Torr pressure was used in the reaction, which involved temperatures of the order of 630°C. Samples

TABLE XIII

MATERIAL COSTS FOR POLYMERIC MEDIA
AND ALTERNATE FIXATION OR STORAGE METHODS

Medium	Polymer Weight/kg Water Disposed	Cost/ kg Water	Cost/ Gallon Water
Resorcinol-formaldehyde acetaldehyde polymer	5.9 kg	$ 4.50	$16.90
Phenol-formaldehyde-acetaldehyde polymer	5.6	2.20	8.25
Polyacrylonitrile	2.9	1.60	5.90
Polystyrene	$\geq$2.0	2.20	8.25
Polyacetylene	1.5	0.80	3.10
Polyureylene/polymethane		12.00	43.00
Polymer impregnated concrete	5.2-5.5	5.27	19.00
Isotope separation[(a)]	---	0.18-0.23	0.68-0.87

[(a)] Isotopic concentration of ^{3}H by a factor of 100.

Sources: References 37, 39, 41, 42 and 43.

of irradiated zircalloy 2 and zircalloy 4 cladding from nuclear reactors were also found adequate for hydrogen storage. There appears to be practically no combustion hazard for zirconium hydride.[45]

Results have been obtained of tritium leach tests on zirconium hydride in various solutions extending over a period of 1 year (Table XIV)[34]. There was no detectable release during the first 6 months. During the period from the sixth to the twelfth month, releases of 2.3 x 10^{-5} to 6 x 10^{-5} (for distilled water) and 1.6 x 10^{-4} (for HCl) of the tritium inventory were measured. In another case (NaOH solution), the zirconium hydride sample fell to the bottom of the vessel during the sixth month and was crushed by the stirring bar. Subsequent to this accident, which greatly increased the surface to volume ratio, the fraction of activity released in the next 6 month period was 5.5 x 10^{-4} of the initial tritium inventory. It appears that hydrides are an adequate storage medium for tritium, yielding small leak rates.

The atomic weight of Zr is 30 times that of H-3. It has been shown that each atom of Zr can adsorb between 1.5 and 2 tritium atoms. Thus the weight of zirconium needed to fix tritium is in the range 15 to 20 times the weight of tritium to be fixed. One curie of tritium weighs 1.03 x 10^{-4} grams as T_2. One curie weighs 1.37 x 10^{-4} grams as HT. Assuming that 10 reprocessing plants are operating in the U.S. and generating comprehensively 1.25 x 10^7 Ci/year, the weight of tritium released would be 1.3 kg/year. This amount of

TABLE XIV

TRITIUM ACTIVITY IN LEACH SOLUTIONS ZrH_x (T)

Control Solutions (No T)	Counts per Min. per ml of Liquid*			
	6/1/74	6/13/74	10/1/74	6/17/75
Distilled Water	31.4	31.5	31.5	37.7
Sat. KCl	35.6	--	--	--
Sat. NaCl	35.5	--	--	--
Test Solutions				
Sat. KCl	--	35.5	--	--
HCl (pH 4)	--	31.8	31.8	53.1
Dist. H_2O	--	31.8	31.6	34.7
Dist. H_2O	--	30.4	30.9	40.0
NaOH (pH 11)	--	30.9	31.3	103.3**
Sat. NaCl	--	35.8	--	--

*Total Tritium inventory equivalent to 1.3×10^5 CPM/ml

**Sample pulverized after October 1, 1974.

Source: Colombo (1975), reference 36

tritium could be fixed with 20 to 26 kg of zirconium, but to achieve this practically all tritium should be in chemically pure gaseous form. In practice most of the waste is tritiated water mixed with ordinary water from which it is impractical to chemically and isotopically separate the tritium. In those cases where the tritium can be isolated, fixation in hydrides appears to be very promising.

4.3 Krypton-85

As a result of collection procedures, krypton gas would be available in almost pure form, with at most a small admixture of xenon. The gas can be immobilized by a number of physical and chemical fixation technologies being developed.

4.3.1 Pressure Vessel Containment

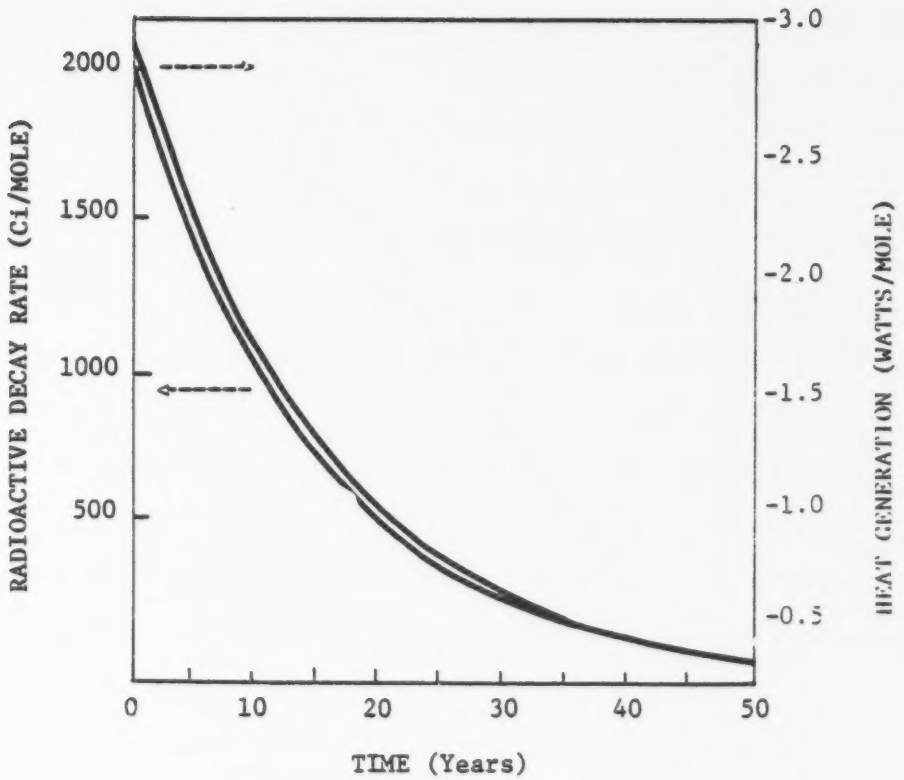
One technology that already exists is the pressurized cylinder which has been used to store compressed industrial gas for at least 50 years.[46] Several thousand of these cylinders have been tested by Union Carbide in normal usage over many years and extrapolation of their results indicates a useful life of 500 years. It was learned from Union Carbide that current use of as many as 5 million cylinders indicates that their failure rate, including leakage, is probably far less than the rate of one in 500 per year, thus the 500 year life can be regarded as a minimum.[47] This assumes, however, normal room-temperature use. For long term storage of Kr-85, it is estimated that a period of 100 years is sufficient in that the krypton released would be a small fraction of the allowable quantity in 40 CFR 190. However,

the steady radioactive decay would liberate an appreciable amount of thermal energy. Figure 6 shows the course of this heat generation in a mole (85 gms) of Kr-85 or about 1.42 kg (375 liters) of krypton gas with a 6 percent Kr-85 constituent.[48]

The low-alloy high-strength steels used for high pressure cylinders exhibit strain aging in the temperature range 150 to 370°C. that results in a tensile strength increase. However, above 370°C., the yield and tensile strength decrease with increasing temperature. Hence, the maximum temperature of the storage cylinders must be held well below 370°C.

Estimates of the storage capacity were made under the assumption of presently available technology.[46] Heat transfer was calculated for cylinders, cooled only by natural convection (21°C ambient air), containing 6.0 percent Kr-85 in krypton gas. The results for 50-liter volume cylinders are shown in Table XV.

The number of storage cylinders required for the annual krypton production from the 1500 metric ton/yr model reprocessing plant is 100 at 500 psi and 29 at 2000 psi.[13] At 500 psi, 12800 curies of Kr-85 are contained in each cylinder and at 2000 psi 41900 curies of Kr-85 are contained in each cylinder. Hence, the higher pressure poses a greater adverse effect associated with the risk of cylinder failure. At the higher pressure, between 1500 and 2000 such cylinders could be in use by the year 2000. If there is an admixture of 25 percent xenon by volume in the gas as anticipated, these estimates would be raised by one-third.



Source: Christensen, Reference 48.

FIGURE 6
KRYPTON-85 HEAT GENERATION AND DECAY RATES AS A FUNCTION OF TIME

TABLE XV

ANNUAL Kr-85 STORAGE REQUIREMENTS
FOR A 1500 MT/YEAR REPROCESSING PLANT

Storage Method	Pressure Psi	Amount of Sodalite Kg	Storage Temp. °C	Number of 50 liter Cylinders
	500		60*	100
Pressured Cylinder	2000		127*	29
Sodalite Encapsulation+		2800	120++	82

*Wall temperature

+Assumed loading 1.8×10^{-3} mole (40 ml STP) Kr per gram of sodalite

++Mean temperature: Center-line temperature is 150°C

An uncertain danger posed by simple gas storage is the steady accumulation of the alkali metal rubidium, the Kr-85 decay product. Table XVI indicates rubidium production of 327 gm and 1070 gm, respectively, in the 500 psi and 2000 psi cylinders after 150 years' decay. As long as the cylinder is intact, the inert krypton atmosphere will prevent the rubidium chemical reactions to which it is normally prone when in contact with moisture or O_2. However, the liquid rubidium may still attack the steel of the cylinder by removing carbon and nitrogen from the grain boundaries. This effect has been identified for liquid sodium in the stainless steel tubes of LMFBR cooling system, but these effects are detectable only at temperatures above 450°C. Hence there is a reasonable likelihood that at the low storage temperatures which define mechanical stability for the cylinders, the chemical corrosion danger of rubidium will be absent. By the same token, the danger of excessive temperatures poses a hazard both in the potential for chemical reactions by the rubidium and the increased risk of containment failure through increased pressure.

4.3.2 Zeolite Adsorption

Additional safety benefits such as sharply reduced adverse effects of a cylinder failure and lower storage costs are obtained if krypton is immobilized in a solid form prior to encapsulation. Containment of krypton in zeolites has reached an advanced stage of development for this purpose.

Table XVI

RUBIDIUM PRODUCTION DURING STORAGE OF KR-85
IN HIGH PRESSURE STEEL CYLINDERS

Year	500 psi cylinder			2000 psi cylinder		
	Kr-85 (Ci)	Rb (g)	T (°C)	Kr-85 (Ci)	Rb (g)	T (°C)
0	128,000	0	60	419,000	0	127
10	67,200	155	45	220,000	509	84
25	25,600	262	32	83,800	857	50
50	5,090	314	24	16,700	1030	21
100	294	327	21	6,660	1070	25
150	8	327	21	27	1070	21

A zeolite suitable for krypton is basic sodalite which normally contains some NaOH as part of the crystalline atomic array. Its formula is:

$$Na_6 (Al_6Si_6O_{24}) \times NaOH \cdot (8 - 2x) H_2O$$

with each NaOH replacing 2 H_2O molecules of the ideal sodalite hydrate. The sodalite interstitial cages (Figure 7) for krypton sites are truncated octahedra with about, 6.6 Å free diameter for an inscribed sphere. At room temperature, the krypton atom occupying the site has a diameter which can be inferred from classical gas theory to be 3.5 Å. The "cage" site position represents a relatively strong free energy minimum for the krypton atom in the zeolite crystal lattice. Activation energy for mobility of the atom across cage sites is high enough so that after diffusion of krypton into the lattice at the moderately elevated temperature range of 300°-400°C, the krypton is effectively trapped when the zeolite crystal is quenched below 150°C. Storage requirements for this kind of krypton immobilization have been compared to those for the pressurized steel cylinder in Table XV.[49]

The process of loading krypton into a zeolite is shown in Figure 8.[13] Activated zeolite (interstitial water removed) is loaded into the pressure vessel and heated to the adsorption temperature. Krypton is introduced from a cylinder at the encapsulation temperature, the temperature is lowered after the desired approach to equilibrium adsorption in the zeolite, and the unadsorbed krypton is left in the

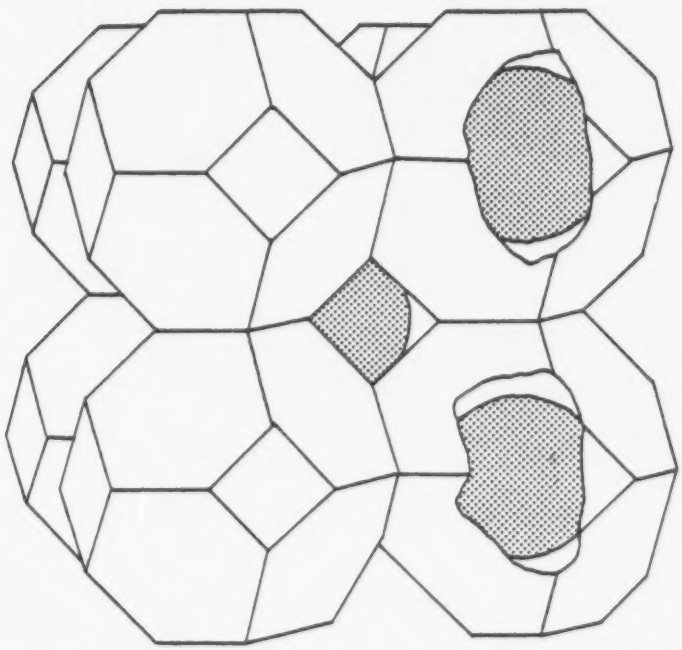
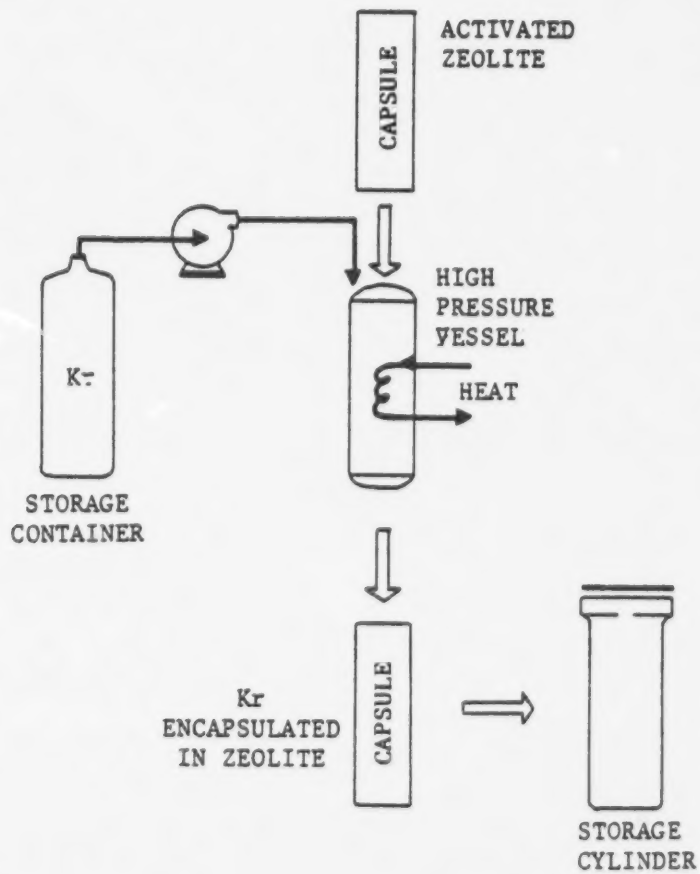


FIGURE 7
REPRESENTATION OF SODALITE CAGES
CONTAINING KRYPTON ATOMS



Source: Knecht, Reference 13.

FIGURE 8
PROCESS FOR HIGH PRESSURE ENCAPSULATION OF Kr IN ZEOLITE

storage cylinder. Tests are being conducted on this process to determine the amount of krypton gas which can be so encapsulated as a function of time, pressure, and temperature, and also to determine the leakage rate for inference of leakage at storage temperatures over long periods of time. The most obvious physical advantage of this kind of trapping in a solid is the continued isolation of the possibly corrosive rubidium decay product.

If one krypton atom occupies each cage of sodalite, the saturation capacity for ideal sodalites is 52.6 cm^3 (at STP) of krypton gas per anhydrous gram of sodalite. Tests of equilibrium isotherms of Kr, as a function of pressure for the amount of Kr sorbed on sodalite, conform closely to the shape of the Langmuir formula for fraction of saturation capacity sorbed in a perfect sorbent. Test data at diffusion temperatures between 326°C and 544°C[49] indicated a saturation sorbency of 45 cm^3/gm, in fair agreement with the theoretical value. The results were similar both for sodalite with intercalated NaOH and for the NaOH removed by extraction. The equilibrium capacities did not change, indicating that krypton could occupy a cage containing NaOH. It is therefore anticipated that 1 kg of zeolite can trap 45 liters of krypton at STP for a total requirement of 3180 kg/year zeolite for one reprocessing plant.

Diffusion data at high temperatures was used to measure the activation energy and diffusion constant to evaluate that leakage

rates at low temperatures. For a fractional leakage Q_t/Q_∞ at temperature T, the diffusivity:

$$D = \frac{\pi r_o^2}{36} \cdot \frac{d\left(Q_t/Q_\infty\right)^2}{dt}$$

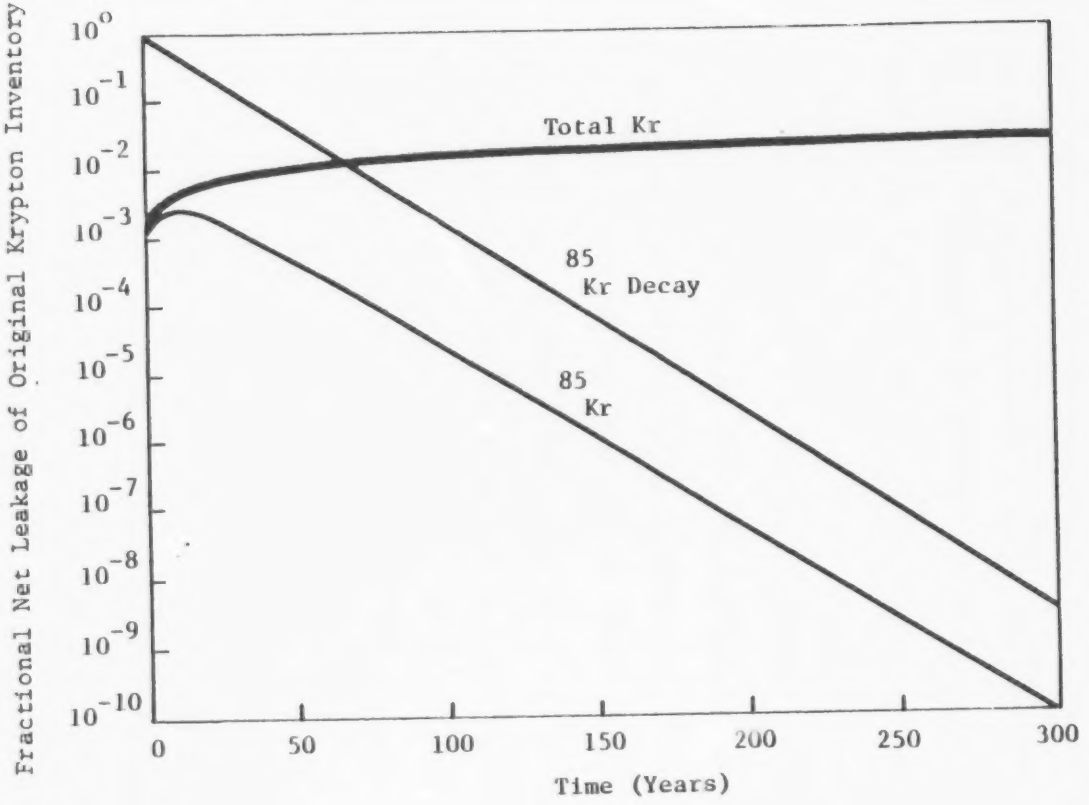
where r_o is an average diffusion path length related to the size of zeolite or sodalite crystals (Q_t = quantity diffused in time t; Q_∞ = quantity diffused after an elapse of an infinite period). The values of Q_t/Q_∞ were measured as a function of time at temperatures between 413°C and 560°C for a number of samples using a mass spectrometer to detect the leakage of krypton. This determines the temperature dependence of D which indicates both the diffusion constant D_o and the activation energy E via the equation.

$$D = D_o \exp\ (-E/RT)$$

were then used to calculate the long term leakage at 150°C shown in Figure 9. The graph shows the effect of radioactive decay of the entrapped krypton upon the leakage of the radioactive species from the sodalite. The shape of the curve for Kr-85 is represented by the equation

$$\left(Q_t/Q_\infty\right)_{Kr\text{-}85} = 6\left(\frac{D_o t}{\pi r_o}\right)^{1/2} \cdot \exp\left(-\frac{E}{RT} - \lambda t\right)$$

where the factor $\exp(-\lambda t)$ accounts for radioactive decay. The fractional leakage of krypton at 150°C and 100 yrs is 2×10^{-2}. If the cylinder containing sodalite ruptures at this time due



Source: Knecht, ICP-1125, Reference 13.

FIGURE 9
CALCULATED RELEASE OF ORIGINAL KRYPTON INVENTORY FROM SODALITE AT 150°C AS A FUNCTION OF TIME

to Kr-85 decay, only 3×10^{-5} of the original Kr-85 will escape. This is shown on the Kr-85 line. After eight years the fractional net leakage of Kr-85 is a maximum of 3×10^{-3}, which represents a safety factor of 200 for sodalite encapsulation relative to pressurized tank storage.

4.3.3 Ion Implantation/Sputtering

Another method for immobilization of krypton in a solid is ion implantation or sputtering on crystalline or amorphous solids.[13] Krypton can diffuse into a metal surface (at high temperature and pressure) to a depth of $\leq 10^{-5}$ cm and occupy a lattice position.[15] At loadings far below saturation, the amount of Kr sorbed, V, varies linearly with:

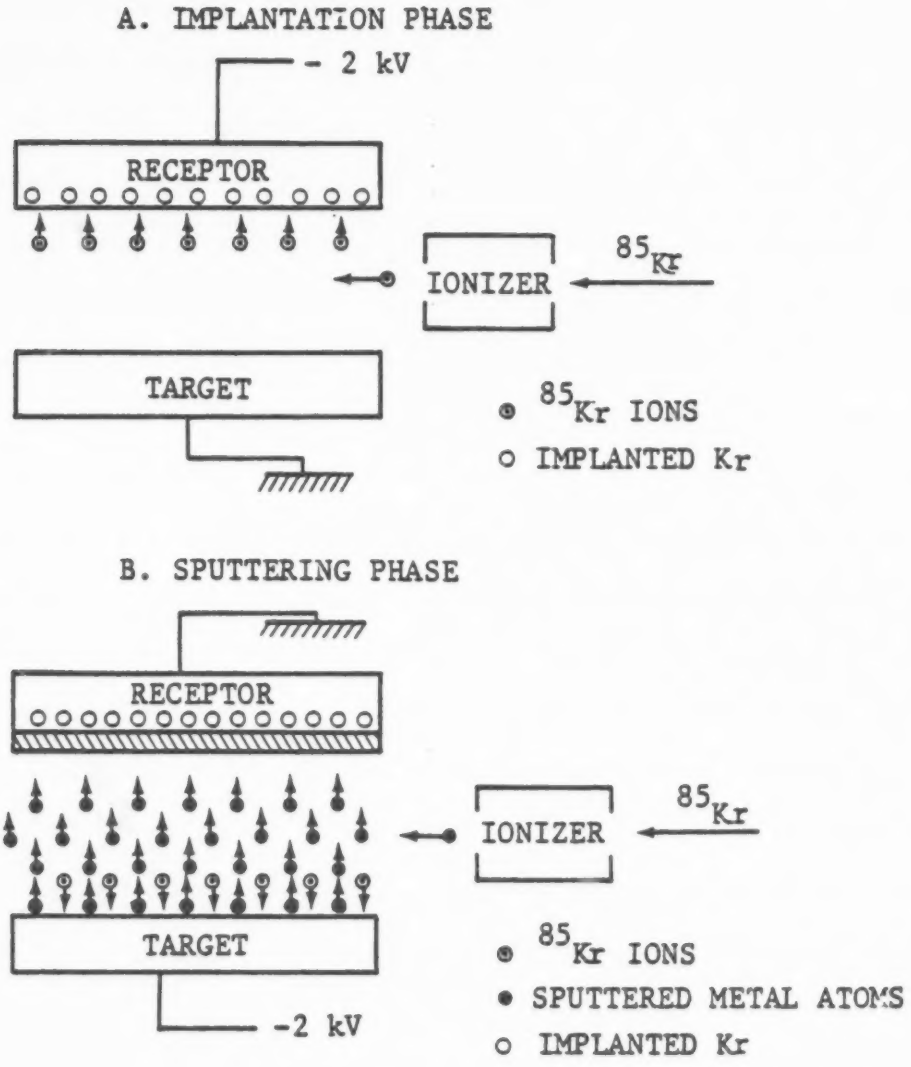
- pressure
- t, where t is time
- exp (1/T), where T is the temperature

More than 25 different powders, foils, and other solid forms have been used to sorb krypton (including copper, aluminum, iron, nickel, gold, silver, etc.). Loadings achieved at tens of megapascals* (200-800°C and 5-90 hours) were typically far from equilibrium in the range 10^{-2} to 10^{-6} cm^3 g^{-1}. Tests at the Idaho National Engineering Laboratory (INEL) using $\frac{1}{4} \times 10^{-6}$ meter aluminum powder at 510°C, 190 MPa** and 24 hours resulted in less than 1 cm^3 g^{-1} loading.

*Pascal (Pa) = Newton/$meter^2$
**MPa = 10^6 Pa

The results of the INEL test are shown in Table XVII. Total amounts of metal required are in the range of millions to billions of metric tons.

In high temperature/high pressure sorption, krypton is imbedded by diffusing into a solid under a concentration gradient. An alternate method of imbedding krypton uses electrostatic energy to accelerate krypton ions (at low pressures, 0.1 to 100 Pa) into a receptor surface as shown in Figure 10.[50] After the receptor surface has been loaded, the polarity can be reversed and krypton ions are accelerated to strike a target surface. The metal atoms which are sputtered from the target by the energy of ion bombardment are deposited on the receptor, yielding a "clean" surface into which additional Kr ions can be implanted. The process can be operated to maximize implantation in one target and sputtering in the other. The trapping efficiency is a function of Kr ion penetration in the receptor and of the probability that the Kr ion is accommodated in the crystal structure (in voids or vacancies) and increases with increasing energy, approaching a maximum in the kilovolt region. The atomic number and structure of the substrate have a variable effect on trapping, and its temperature has an inverse effect on trapping. Purity requirements of krypton have not yet been determined; potential effects of the xenon impurity must be measured. Xe with ionization potential of 12.1 eV can interact with krypton ions (Kr ionization potential is I4.0 eV) resulting in xenon ions and krypton atoms; since Kr must be in ionic form to be trapped, a decrease in efficiency could occur.



Source: Check, et.al., Reference 50.

FIGURE 10
PROCESS FOR IMMOBILIZING ^{85}Kr BY ION IMPLANTATION/SPUTTERING

TABLE XVII

SORPTION OF KRYPTON GAS BY METAL

Metal	Process	Wt.-Fract. Loading	Required Wt. of Metal*
Cu Al Fe Ni Au Ag	Diffusion under high temperature and pressure 10 100 MPa+ 800°C 5 90 hrs.	3.7×10^{-5} to 3.7×10^{-8}	1.4×10^{6} Tons to 1.4×10^{9} Tons
Ni	Ion Implantation/Sputtering at low pressures (.1 100 Pa)	5.98×10^{-2}	8.91 Tons
$Gd_{.11}Co_{.73}Mo_{.16}$	"	.475	1.12 Tons

*Required for 1500 Mg/yr reporcessing

+Meghpascal = MPA = 10^6 N/m^2 = 9.87 atmospheres

Studies of this method of trapping Kr-85 are underway in foreign countries (including the U.K. and Germany) as well as in the U.S. at Battelle-Pacific Northwest Laboratories. Loadings of up to 4 atom percent (16 STP cm^3 Kr g^{-1}) in kilogram quantities of Ni have been achieved at Battelle using a high density sputtering system. Higher loadings (of up to 30 atom percent or 127 cm^3 g^{-1}) have been achieved in thin films of the amorphous material, $Gd_{0.11} \cdot Co_{0.73} \cdot Mo_{0.16}$, possibly due to the pressure of larger interstitial voids in the disordered materials. As indicated in Table XVII, for both of these cases the total weight required for each reprocessing plant is only a few metric tons.

Other Immobilization Technologies

Since metals have a large thermal conductivity, good mechanical strength, and high radiation resistance, they have been used to form matrices containing high-level wastes. One possible process for forming a metal matrix uses molten metal casting. Metal matrices that have been formed by this process contain different combinations of calcine with aluminum, iron, zinc, lead-tin, aluminum-titanium, or iron-titanium.[52] The metal matrix volume is about the same as the volume of the calcine. Metal matrices have also been formed by compacting a mixture of calcine and metal powders and then sintering the mixture. Both processes form products with compression strengths above 26.7 MPa and thermal conductivities 10 to 60 times that of glass matrices. However, the process temperatures range between 280°C and

980°C. As with glass, the high temperatures (>400°C) of the molten metal casting process are not suitable for immobilizing solids containing krypton. It has been speculated that if metals with low melting points are used,[53] the sintering process could advantageously immobilize granules containing krypton.

4.4 Carbon-14

The only technique currently being studied for the immobilization of C-14 is the formation of calcium carbonate ($CaCO_3$) and subsequent incorporation into concrete or other material.

4.4.1 Concreted $CaCO_3$

The concreted $CaCO_3$ product can be considered to be low specific activity (LSA) material. Such materials have only the very minimum of package requirements, usually referred to as Type A, which can use a wide varity of readily available metal or fiber drums, wooden boxes or fiberboard boxes, and must meet conditions principally consisting of various drop tests.

The concrete holds about 30 weight percent $CaCO_3$. Thus the annual output of 1.36 kg $CaCO_3$ from a model reprocessing plant will be incorporated in 4.5 kg of concrete ($0.003 m^3$) as a yet undetermined multiplication factor due to the absorption of carbon from the atmosphere which would raise this by a factor between 1 to 100.

The standard 55-gallon steel drums (which sell for about $10 each) would seem to satisfy the Type A packaging requirement for $CaCO_3$ containing the radioactive C-14. The concretion of $CaCO_3$

and packaging in steel drums has been estimated to cost approximately 40 cents/gallon or approximately $\$1.00/m^3$.

4.4.2 Leaching of C-14 from Concrete

Experimental data for the leaching of C-14 from concreted $CaCO_3$ are not available. However, the solubility of $CaCO_3$ in pure water is about 1.4×10^{-7} kg mole/litre. This is about a fifth of the value for $BaIO_3$, whose leaching properties were discussed in section 4.1.

5.0 DISPOSAL OPTIONS FOR VOLATILE RADIONUCLIDES

Radioactive waste is the inevitable byproduct of nuclear electric power generation. The annual projected nuclear power capacity in the U.S. varies from 400 to 1000 GWe by the year 2010. While radioactivity is encountered at most stages of the nuclear fuel cycle, the largest quantities and those of potentially greatest concern are those present in spent fuels. Using the projected nuclear capacity in the U.S. by the year 2010, the corresponding commercial waste burden of spent fuel is estimated to be between 3.1 and 7.7 x 10^5 metric tons of heavy metal (MTHM) per year.[2]

Under the reprocessing option, spent fuel elements from nuclear reactors are reprocessed to recover usable uranium and plutonium. During these chemical processing operations, radioactive particles and volatile materials are released to the off-gas effluent streams. Control approaches have been utilized by the nuclear industry to maintain radiation emmission levels of these volatile radionuclides below applicable standards. Although present control technology is capable of meeting or exceeding required standards, the disposal of volatile radionuclides which will be produced in evergrowing quantities will be a matter of concern.

The primary source of volatile radionuclide release in the nuclear fuel cycle is spent fuel reprocessing operations. The

exception to this would be in the case of U.S. policy decision not to perform reprocessing and to directly dispose of spent fuel elements without recovery of uranium or plutonium. In this event, the primary release of the volatile radionuclides would occur sometime after disposal if the integrity of the fuel elements and other engineered containment barriers were to fail.

5.1 Disposal Concepts

In previous sections various methods of collecting and immobilizing volatile nuclides were discussed from a technical and environmental impact perspective. This section discusses final disposal options which are feasible for volatile radionuclides. A brief description of each disposal option is summarized below. Radioactive waste disposal options are discussed in detail in references 3 and 54.

5.1.1 Geological Repository

Disposal of radioactive wastes in deep, stable geologic formations has long been the preferred method for isolation of wastes from contact with man's environment. A number of possible geologic media have been considered for such disposal. These include salt beds, salt domes, crystalline rock forms such as granite or basalt, shales, limestones, and certain types of clay beds. To date, salt deposits have received the most attention as a suitable medium, especially in the U.S., because of their demonstrated stability over very long

time periods, their homogeneity, and their property of plastic flow and selfhealing in the presence of stress. The self-healing properties of salt effectively eliminate the possibility of extensive cracking, thereby preventing the opening of pathways to radionuclide migration in the environment.

An alternative to salt is stable crystalline rock, such as basalt or granite. Again, crystalline rock is a suitable candidate with demonstrated seismic stability. Crystalline rock, however, does not have the self-healing characteristics of salt but possesses other advantages, including resistance to water intrusion, that make it a desirable medium for geologic disposal of radioactive waste.

Shales and clay deposits have also been considered for geologic disposal. They have the advantage of low water permeability, but the disadvantage of indeterminate long term stability characteristics.

The effectiveness of geological repositories to isolate volatile radionuclides depends on two factors:

(1) the form of the waste material and its resistance to transport;

(2) the location and design of the geologic disposal facility to achieve maximum isolation from the environment.

More specifically, there are several important factors which determine the effectiveness of geological repositories to isolate the

volatile radionuclides:

- the form of the waste products
- the type of containment
- the resistance of the waste matrix to leaching
- the solubility of the leached radioactive elements in ground water

All of these factors affect the rate at which water might transport radioactivity from the repository.

To date, the major thrust of analyses of engineering controls of geological repositories has been limited to salt deposits, because this is the only type of geological medium for which extensive information is available and because of their demonstrated stability for long periods of time. For other media such as shale, basalt, or granite, the data available are limited in scope.

The greatest concern for the migration of volatile radionuclides through the geosphere to areas of immediate significance to mankind appears to be related to groundwater movement. The initial groundwater flow conditions at potential disposal sites of geological resposítories are extremely important. The leaching characteristics of volatile radionuclides are also important to the migration route.

5.1.2 Seabed Disposal

Seabed disposal involves the controlled emplacement of volative radionuclides in deep sea sediments or beneath the bedrock of the ocean floor. The effectiveness of seabed disposal in containing volatile radionuclides depends upon demonstrating that seabed

emplacement can contain the volatile radionuclides long enough for them to decay to relatively innocuous levels.

Under the seabed, physical and environmental barriers exist that may prevent the migration of radionuclides to parts of the ocean that are of immediate significance to mankind. On the other hand, several mechanisms may act singly or in combination to compromise the integrity of the physical and environmental barriers:

- corrosion of the canister;
- leaching of the waste material;
- upward transport through the upper sediment layers to the lowest water layers;
- advection and diffusion through the water column;
- biological transport of incorporated isotopes across the seabed or upward through the water column.

For seabed disposal, it is crucial to select an ocean repository which has demonstrated geological stability and which consists of deep sea sediments that can act as an effective barrier to isotope migration for geological time periods. These requirements are especially crucial for I-129 and C-14 because of their long half-lives.

5.1.3 Transmutation

One of the possible alternatives being considered for the management of long-lived radioactive wastes is to transmute them into short-lived or stable isotopes. If this concept is demostrated to be

technically feasible, the quantity of waste containing long-lived radionuclides could be reduced significantly, and the time required for the storage of the waste shortened.

The process of transmutation is accomplished by using some nuclear device. Four types of such devices have been discussed in the literature: particle accelerators, thermonuclear or fission explosives, fusion reactors, and fission reactors. Each type of device has to be judged on several criteria including overall energy balance, overall waste balance, and the rate of transmutation. A favorable overall energy balance implies that the energy required to dispose of the waste should be less than the energy furnished by the reactor which produced the waste, preferably by an order of magnitude or better. A conceivable exception would be when the era of nuclear fission power comes to an end and there are other plentiful energy sources available which can be used for the disposal of wastes left over from that era. The criterion of overall waste balance is self-evident: the waste disposal program should not create more waste than it removes. The rate of transmutation depends not only on the particular device that is utilized, but also the properties of the target nuclides.

5.1.4 Extraterrestrial Disposal

The concept of extraterrestrial disposal involves launching radioactive nuclear waste into space or for placement on planetary

bodies without any possibility of return to earth. The long-lived wastes, with half-lives of thousands to millions of years, may thus be disposed of without concern for the lifetime integrity of their containers and respositories.

Extraterrestrial disposal is expensive. The feasibility of using it for the disposal of tritium and Kr-85 may be questionable because these isotopes have relatively short half-lives and other disposal options may be more practical. Containment for a period of about 200 years may be adequate to ensure that these volatile nuclides decay to relatively innoccous levels.

Both I-129 and C-14 have lifetimes which are long enough to warrant consideration of methods of disposal other than long term containment. Therefore, space disposal should be considered as a possibility for the disposal of I-129 and C-14. At the same time, it must be mentioned that the estimated levels of exposure from the possible release of C-14 from the nuclear power industry are of low magnitude and extreme measures to limit its release may not be implemented. Thus, it would appear that among the volatile radionuclides, I-129 alone should be seriously considered as a candidate for space disposal at the present time.

By far the most serious concern associated with space disposal involves launching accidents and space vehicle re-entry. An accident involving concentrated amounts of C-14 and I-129 could pose radiation contamination hazards to man and the environment.

5.1.5 Other Continental Disposal Options

Disposal of radioactive wastes in deep, stable geologic formations is currently the preferred method for isolation of these wastes from contact with man's environment. However, there are alternative concepts to deep geological respositories which are under consideration for different forms of radioactive waste:

- solution mined cavities
- waste disposal in a matrix of drilled holes
- waste disposal in super deep holes
- deep well injection
- hydrofracture

Long term containment is a major concern in the disposal of the volative radionuclides and must be assured in all concepts. The major threat to long term containment is groundwater movement. The concepts must preclude contact of the waste with groundwater movement to minimize waste migration to the biosphere.

Of the alternative geological disposal concepts considered, the technology for super-deep holes is not yet developed and the specific heat of the volatile radionuclides is insufficient for the rock melting concepts. The remaining concepts could have application to the disposal of those radionuclides.

5.1.6 Ice Sheet Disposal

Continental ice sheets have been considered as an alternative approach to the final disposal of high-level radioactive waste.

Theoretically, ice sheets could provide the necessary geographic isolation for some of the short-lived fission product wastes, however, the feasibility of ice sheets' long term containment capabilities is presently uncertain. Before ice sheets could seriously be considered for waste disposal applications, certain areas should be further investigated:

- the evolutionary processes in ice sheets;
- the relationships of ice sheets with climatic changes;
- the effect of future climatic changes on the stability of ice sheets.

Because of these factors, ice sheet disposal will not be considered as a feasible alternative for the disposal of the volatile radionuclides in this report.

5.2 Disposal Alternatives for Volative Radionuclides

5.2.1 Iodine-129

Iodine-129 is produced in the nuclear fuel elements as a fission product and from the radioactive decay of other short-lived fission products. The projected annual release of I-129 from spent fuel in a 1500 Mt/yr model reprocessing plant is 380 kg (66 curies). The half-life of I-129 is 1.7×10^7 years. It would take approximately 1.7×10^8 year (10 half-lives) for I-129 to decay to a low level (i.e., less than 0.1 percent of its original activity).

The chemical waste form and encapsulation technology of I-129 depends upon the designated disposal alternative. Currently,

three processes have been investigated for the collection of iodine: the Mercurex process, the Iodox process, and chemisorption process. These processes chemically combine radioactive iodine into several iodide and iodate compounds. It is important to select an iodide or iodate compound which has demonstrated low leachability. Among these compounds--mercurous iodate, barium iodate, and zeolite--each mixed with concrete has been shown to have fairly low leach rates.

With respect to iodine leaching from concrete, the rate at which water penetrates concrete is slow. Since only a small fraction of the radioiodine compound is in contact with water at a given time at the solid/liquid interface inside the concrete, the dissolution rate of radioiodine is predicted to be slow. Experiments have indicated that 600 kg of iodine in the form of barium iodate incorporated in a concrete cube side of 1.4 meters would leach completely after approximately 1.6×10^4 years. This time period is only one thousandth of the half-life of I-129 (1.6×10^7 years) and as such, over 99.9 percent of the I-129 activity would exist at the time of complete leaching from the concrete. Data on probable periods for complete leaching of other compounds in concrete is not available, but it can reasonably be assumed that the immobilization form of I-129 would be insufficient containment, and additional barriers are required.

5.2.1.1 Geological Disposal of I-129. If I-129 wastes were to be disposed of in a geological repository, it is very important to have minimal or no natural water movement in the strata and interbeds

of any geologic formation. Since it is highly probable that in deep geological repositories there will be water-bearing strata either above or below the potential repository area, water movement in the potential repository strata and interbedded strata will occur. Even if highly selective siting criteria are applied, there can be extremely slow natural migration of water through the repository strata.

Because iodine is not sorbed in ground strata as well as other radionuclides (it has a retardation factor of 1) and because of the long half-life of I-129, there is some concern that geological repositories may not serve as adequate barriers for I-129, particularly for geological time periods. Most of the I-129 will still exist at the time of complete leaching from the containment and may cause localized radioactive contamination to the land and water food chain systems. The I-129 would, of course, be removed from the human environment during the period it remained in containment and the time required to be transported to the biosphere. Since most of the I-129 would eventually be released, geological repositories cannot be considered to offer permanent isolation of I-129. The acceptability of this concept must, therefore, be determined on the basis of the radiological hazard. The rate of release will be a significant factor in this evaluation.

5.2.1.2 Seabed Disposal. If I-129 wastes were to be emplaced in the ocean sediments, the principal requirement for their effectiveness is that deep sea clay sediments act as a suitable

barrier to I-129 migration for a period long enough for it to decay to relatively innocuous levels. As with geological repositories, I-129 is likely to be incorporated in an iodide or iodate compound in a stable form such as concrete. However, concrete may pose some difficulties concerning its effects on emplacement techniques in the ocean sediments. Specially designed canisters and, accordingly, waste forms, need to be developed which will penetrate the ocean sediments in a manner that will ensure hole closure.

Because of the corrosive nature of sea water, the probable period for containment failure and leaching of I-129 is estimated to be from 100 to 1000 years. This period becomes important if the I-129 waste is mixed with short-lived radionuclides for burial. Most of the heat generated by short-lived radionuclides occurs during the first 1000 years of burial. The heat produced by fission product decay during this time period may be high enough to affect the effectiveness of the waste form and canister as a barrier to migration. In general, if radioactive wastes leach through the canister while the deep sea sediments surrounding the canister are at a high temperature, the thermal and hydraulic gradients created by this temperature may cause rapid upward transport of I-129 through the sediments. If the policy is to isolate I-129 from other wastes and encapsulate and bury the I-129 separately, then this problem is insignificant since the heat generated by I-129 alone is small.

Once I-129 has leached from containment, the two remaining barriers are the deep sea sediments and dispersion into the ocean. Specific information on the migration rate of I-129 in deep sea dediments is not availabie. However, assuming no retardation by the sidiment itself due to sorption, an estimate of the migration time can be obtained based on diffusion of the I-129 through the sediment process. The diffusion time, t, is give by

$$t = \frac{L^2}{D}$$

where

t = diffusion time, see
L = depth of sediment, cm
D = diffusion coefficient cm^2/sec

For a burial depth of 100 meters (1×10^4 cm) and using an average value for deep-sea sediment siffusion coefficient of 3×10^{-6} cm^2/sec.

$$t = \frac{(1 \times 10^4)^2}{3 \times 10^{-6}} = 3.3 \times 10^{13} \text{ sec or } 1 \times 10^6 \text{ years}$$

This estimate does not consider the possibility that a warm canister might produce slow conviction of fluids in the sediment pores resulting in a faster transport of the I-129 to the ocean floor. It is not likely, however, that decay heating from I-129 alone would cause such convection.

After migration through the deep sea clays, I-129 will become dispersed into the ocean. If the assumption is made that all I-129 will become uniformly dispersed in the ocean, then the radiological

effects on aquatic and marine organisms may be small. However, there is the risk that uniform dispersion will not take place, and that the I-129 may become localized in certain regions of the ocean. Under these conditions, marine organisms can accumulate I-129 from contaminated food, water and suspended sediments and can enter man's food chain.

Seabed disposal, like geological repository disposal, may not assure the isolation of the I-129 over the period of time required for this isotope to decay to relatively innocuous levels. Seabed disposal does, however, offer an additional barrier to transport to man. Further, the diluting potential of the sea is such that if highly dispersed, the I-129 from radioactive waste disposal may be significantly less, approximately 1/100, of the total radioactivity in sea water (3×10^{-11} Ci/cm^3). [55]

Seabed disposal is a feasible option for disposal of I-129 in that fully diluted waste would be a small fraction of background but would require an evaluation of the transport pathways to determine a low risk of concentrated exposure to the ecosystem. A low concentration of I-129 could be attained if a low release of I-129 is assured.

Studies have been conducted on the retention of iodine in marine clay soils.[57] The clay fraction constituted 68 percent of the soil and contained minerals such as mica, chlorite, quartz, feldspar, and amphobile. Results showed clearly that at low pH values, iodine is

absorbed on clay particles. This property may be utilized to some extent for the retention of iodine in geological formations as well as a marine environment. Quantitative measurements on various types of clay would be useful.

5.2.1.3 Extraterrestrial Disposal. Extraterrestrial disposal of I-129 is technically feasible. Space disposal offers the long term benefit of permanent disposal of I-129 with no interaction with the ecosystem of the earth. However, two factors must be considered in the overall practicality of this concept: (1) space disposal is expensive relative to other alternatives; and (2) space disposal poses a short term risk of accidents with the potential of radiation release.

Assuming that a suitable waste form and encapsulation can be developed, the major technological concern in extraterrestrial disposal is the potential of accidents. With improved launch vehicles such as the space shuttle and highly developed recovery capabilities in the event of an accident, it is estimated that the probability of loss of a capsule containing the I-129 waste could be reduced to less than 10^{-2}. With highly advanced encapsulation technology, the probability of prompt release of the I-129 from vehicle explosion and fire or intact re-entry could conceivably be in the range of 10^{-5} to 10^{-6}.

The important factors in the extraterrestrial disposal option are the probabilities of accidents and the recovery of the waste capsule in the event of an accident. Whether or not space disposal

represents an acceptable risk with the inherent hazards of uncontrolled loss of a waste package requires a detailed system concept evaluation and risk and consequence assessment. Without such an analysis, the acceptability (aside from economic consideration) of extraterrestrial disposal cannot be determined.

5.2.1.4 Transmutation. Transmutation of I-129 is considered impractical in fission reactors. I-129 has a thermal neutron cross-section of 34.5 barns and an effective fast neutron cross-section of 0.24 barns. At a thermal flux of 3×10^{13} neutrons/cm^2sec, it could take over fifty years to achieve a reduction to 10 percent of the original I-129 activity.

Fusion reactors are capable of producing high neutron flux levels and it is conceivable that these devices could be used to dispose of I-129. The fusion reactor is not developed and requires a major technical breakthrough before this concept can be considered feasible.

5.2.2 Carbon-14

Carbon-14 is in both the fuel elements and the cooling water in light water reactors. At the present time, most of the C-14 in spent fuel is released to the atmosphere as CO_2 during the dissolution of spent fuel at the reprocessing plant. A model 1500 MT/year reprocessing plant releases approximately 0.19 kg of C-14 with an activity level of 850 Ci.

Methods for collection of C-14 from off-gas streams include caustic scrubbing, molecular sieve adsorption, and fluorocarbon adsorption. The most probable chemical form is calcium carbonate, which may subsequently be incorporated into concrete or other materials. The caustic scrubbing method has been shown to remove 99 percent of the CO_2 initially present in the spent fuel and produces $CaCO_3$. Assuming 99 percent recovery of an average 850 Ci of $^{14}CO_2$/year, the average annual output of radioactive calcium carbonate is around 1.36 kg. However, 10 to 100 times as much $CaCO_3$ from atmospheric carbon dioxide would probably be recovered along with $^{14}CO_2$, bringing the total amount of waste to be disposed of per 1500 MT reprocessing plants from 13.6 to 136 kg/yr. The calcium carbonate ($CaCO_3$) is subsequently incorporated into concrete comprising 30 percent $CaCO_3$ and 70 percent concrete. The annual production of 1.36 kg of $CaCO_3$ from a model reprocessing plant is incorporated in 4.5 kg of concrete. Due to the recovery of $CaCO_3$ from atmospheric carbon dioxide, the total amount of concrete containing $CaCO_3$ disposed of is estimated from between 58 to 580 kg/year.

Experimental data for the leaching from concentrated $CaCO_3$ are not available, thus it is difficult to provide estimates on the probable time period for total leaching of $CaCO_3$. It is speculated that this period ranges from 30 to 500 years, depending on the disposal medium. Experiments indicate that if $CaCO_3$ is suspended in

pure water in the presence of CO_2, a small quantity dissolves. If this CO_2 is absent, the $CaCO_3$ progressively decomposes to form $Ca(OH)_2$, which is much more soluble than $CaCO_3$.

C-14 has a half-life of 5.57×10^3 years and will decay to a low level (0.1 percent of original activity) after 5.57×10^4 years. Several disposal options may be applicable to C-14.

5.2.2.1 Transmutation. The transmutation of C-14 in fission reactors is not feasible because the cross-section of carbon-14 for both thermal and fast flux neutrons is of the order of microbarns. Even at a high flux of 10^{17} neutrons/cm^2sec, the transmutation rate is about $10^{-13}sec^{-1}$ compared to the natural decay constant of $10^{-12}sec^{-1}$ for relatively long-lived C-14. Thus transmutation may be ruled out as a disposal option for C-14.

Transmutation in fusion reactors may have some potential, but the future availability of fusion reactors is uncertain.

5.2.2.2 Geological Disposal and Seabed Disposal. Two disposal options appear to be capable of maintaining long term integrity and isolation of $CaCO_3$ wastes: geological disposal and seabed disposal.

For the geological disposal option, the most important barrier to C-14 transport to the geosphere is the proposed salt beds and underground strata. Since it would take approximately 5×10^4 years for C-14 to decay to 0.1 percent of its original activity, it must be demonstrated that geological repositories could potentially

act as an effective barrier for this time period. A large degree of uncertainty is associated with values of the geological parameters important in geosphere transport. All that can be established is a range in values for important parameters. Experiments on the migration potential of C-14 in various media indicate that C-14 is transported fairly rapidly relative to other radionuclides (retardation factor = 10). More experimentation on $CaCO_3$ is necessary to establish quantitative estimates of leach rates, hydrodynamic dispersivity, water migration ratio, and dilution in nuclide concentration that occurs during migration. However, analytical models of geosphere transport indicate that only insignificant amounts of C-14 would be transported to areas of danger to humans during the period C-14 decay to 0.1 percent of original activity.[56] Assuming that the transport models are confirmed, the conclusion is that geological repositories are capable of maintaining integrity and providing isolation of C-14 for the duration of its significant activity.

For seabed disposal of $CaCO_3$, it is important to demonstrate that deep sea sediments (clays) can contain C-14 and prevent migration to the ocean for 5×10^4 years. The retardation factor of the migration of carbon has not as yet been determined. It is likely, however, that deep sea clays will act as an effective barrier to C-14 migration. The potential problems of containment in the seabed as previously discussed also apply to C-14. Further research and development is obviously required to support the concept of seabed disposal.

5.2.2.3 Extraterrestrial Disposal. Extraterrestrial disposal of C-14 is technically feasible. Space disposal offers the long term benefit of permanent disposal of C-14 but with a short term risk of some accidental release as discussed for I-129. The costs of space disposal are high compared to geological and seabed disposal. If these latter alternatives are shown to be effective in isolating C-14 wastes, is no overriding reason to recommend that C-14 be disposed of in space.

5.2.3 Tritium

Tritium is produced in fuel elements, control rods, and in the primary coolant of light water reactors. The tritium contained in fuel elements will be treated at reprocessing plants and disposed of accordingly. A model 1500 MT/year reprocessing plant releases approximately 3×10^4 kg of tritiated water from the voloxidation method with an activity level of 1.06×10^6 Ci.

Because tritium has a relatively short half-life (12.3 years), it can either be stored above ground in large cylinders or chemically treated for final disposition. For final disposition, a probable waste form is polymer impregnated tritiated concrete (PITC). Based on a polymer weight/kg of tritiated water of 0.5, the total amount of PITC which will be disposed of is 1.5×10^5 kg/year (based on a 1500 MT/year reprocessing plant). For storage, unaltered tritiated water must be contained for approximately 200 years (it takes 191 years for 1×10^{-3} Ci/liter of tritiated water to decay to the

allowable drinking water concentration of 2×10^{-8} ci/l (20,000 pci/l). Leach experiments have indicated that the probable period for total leaching of PITC ranges from 30 to 200 years.

5.2.3.1 Geological and Seabed Disposal. Because of the relatively short half-life of tritium, both geological and seabed disposal provide adequate barriers to migration for periods long enough to allow tritium to decay to relatively innocuous levels. This occurs after approximately 200 years.

Tritium reacts very little or not at all with sediments and soils (retardation factor = 1). Even if there is total leaching of PITC within 30 years, the decay period for active tritium is small compared to the time period it would take tritium to migrate to areas of significance to man from deep geologic or seabed disposal. It decays before it reaches the biosphere. It is desirable to isolate the tritium from other waste simply to avoid an additional water source which could accelerate leaching of other emplaced waste.

For seabed disposal, deep sea clays act as an effective barrier to migration of tritium. It is postulated that it would take tritium buried 100 meters below the deep sea sediments approximately 10^5 years to migrate to the ocean surface. This time period is far greater than the time necessary for tritium to decay to relatively innocuous levels.

5.2.3.2 Transmutation. The transmutation of tritium is not feasible because the cross-sections for both thermal and fast flux

neutrons are of the order of microbarns, which is too small to achieve an appreciable gain over tritium's natural decay rate.

Tritium is utilized as a fuel in fusion reactors and could be beneficially used if this technology is developed.

5.2.3.3 Extraterrestrial Disposal. Extraterrestrial disposal of tritium is technically feasible; however, the costs of space disposal would be high compared to geological and seabed disposal. These latter alternatives are more suitable for tritium disposal.

5.2.3.4 Engineered Storage Facilities. The 12.3 year half-life of tritium is such that above ground engineered storage during radioactive decay is feasible. The engineered facility must assure public and occupational safety for normal operation and in the event of accidents. A facility design similar, but of less complexity, to that discussed below for Kr-85 storage (Section 5.2.4.4) would probably be used. Capability for recovery of tritium and repackaging, and decontamination in the event of leaks would be required.

5.2.4 Krypton-85

Krypton-85 is the only noble gas radionuclide formed as a U-235 fission fragment present in appreciable quantities when LWR spent fuel is reprocessed or in unreprocessed spent fuel stored for ten years. The half-life of K-85 is 10.73 years and it takes approximately 100 years for it to decay to 0.1 percent of its original activity. The annual gaseous krypton production from a model

reprocessing plant is about 530 kg, which has a volume of 143 m^3 at standard temperature and pressure. About six percent of this krypton is Kr-85 with an activity level of 1.3×10^7 Ci/year.

A number of methods are being developed for collection of krypton from off-gas streams:

- cryogenic distillation;
- cryogenic selective adsorption;
- fluorocarbon adsorption.

These collection methods are described in detail in other sections of this report. As a result of these collection procedures, krypton gas would be available in almost pure form. One technology that already exists is the containment of krypton gas in pressurized cylinders. Several thousand of these cylinders have been tested in normal usage over many years and extrapolation of their results indicates a useful life of 500 years; however, these tests have been conducted at room temperatures. Radioactive decay of krypton would liberate an appreciable amount of heat. The corrosion properties of the daughter product rubidium must also be determined. Experiments indicate that the alloy steels used for these high pressure cylinders must be held well below 370°C because above this temperature the yield and tensile strength of the cylinders decrease rapidly.

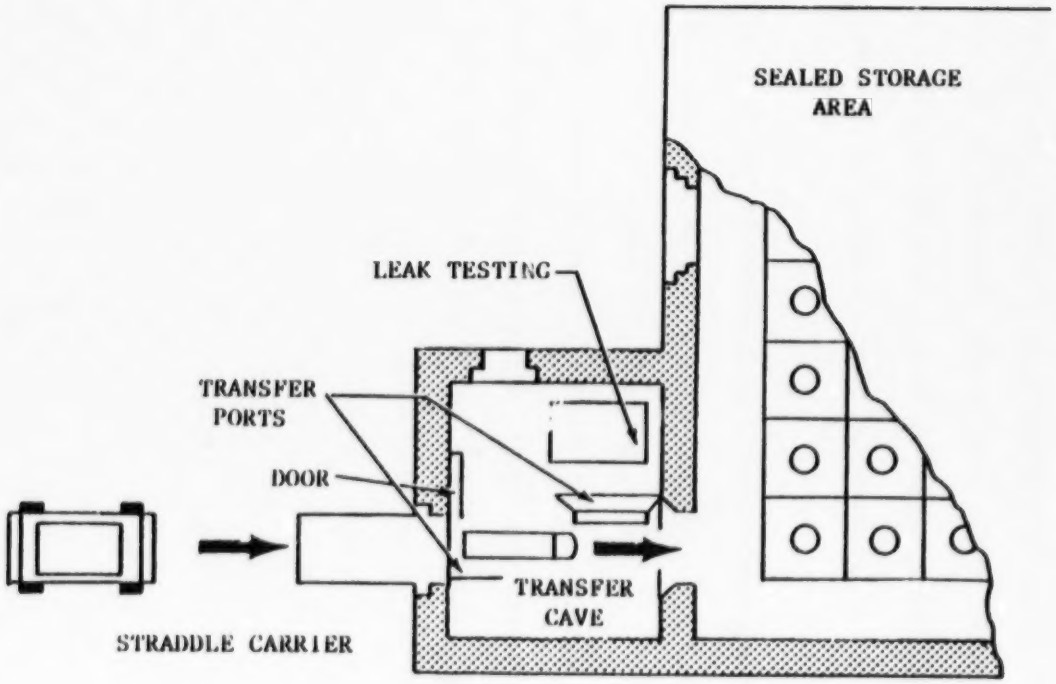
5.2.4.1 Geologic and Seabed Disposal. Because of their relatively short half-lives, both geological and seabed disposal provide adequate protection against migration for periods long enough to allow krypton-85 to decay to relatively innocuous levels. Krypton-85

should be stored separately from high-level radioactive waste to avoid high temperatures which affect containment. Disposal of Kr-85 in a geological repository could present problems if gas leakage occured during the operating phase.

5.2.4.2 Transmutation. Transmutation of Kr-85 is not feasible because its cross-section for both thermal and fast flux neutrons is too small to achieve an appreciable gain over its natural decay rate.

5.2.4.3 Extraterrestrial Disposal. Extraterrestrial disposal of Kr-85 is technically feasible; however the costs of space disposal are high compared to geological and seabed disposal options.

5.2.4.4. Engineered Storage Facilities. The storage time for permanent disposal of krypton-85, as well as tritium, is relatively low (on the order of 100-200 years, i.e., 10 lifetimes). Both steel cylinders and encapsulated zeolites are the two most promising technologies for Kr-85. The principal danger to be avoided is high temperature from the accumulated decay. Accordingly, the engineered storage facility, as illustrated in Figure 11, [48] is of interest for the Kr-85. It consists of two parts, a remote handling transfer cave and a sealed storage area. Pressurized cylinders or encapsulated zeolite units are transported to the cask in a shielded transfer cave and then moved to a storage slot in the sealed storage area. All this is easily accomplished with remote handling equipment and viewing windows. The other method of promise, deposition in metal by ion implantation, requires very simple storage.



SOURCE: Christensen, ICP-1128, Reference 48.

FIGURE 11
PRESSURIZED CYLINDER STORAGE FACILITY FOR ^{85}Kr

The leak tight storage vault prevents any sudden accidental release of Kr-85, if a pressurized cylinder develops a leak. In the event of failure of one or more pressurized cylinders, the released krypton must be confined to the storage facility until it is recycled through an adjoining krypton recovery unit. The encapsulated zeolite is not vulnerable to such release and could be stored in a simpler facility.

The engineered storage option is also attractive in this case because with the decay of Kr-85 it may be useful to retrieve older capsules or cylinders for testing and possible reuse.

Tritium could be stored in a similar type of facility. Large quantities of tritium are required if thermonuclear (fusion) reactors reach the operational stage of development and the tritium waste could, at that time, be gainfully used.

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